H.C
L434

KEY INSPECTION CENTRE

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74638, filed 22nd December 1960. 1 Paus 1882 (Saka) Reciprocity date (United Kingdom) 29th December 1959. (Accepted 3rd February 1962).

" IMPROVEMENTS IN OR RELATING TO ELECTRIC SECONDARY CELL CONTAINERS AND TO ELECTRIC BATTERIES AND CELLS INCLUDING SUCH CONTAINERS. "

OLDHAM & SON LIMITED, A COMPANY INCORPORATED UNDER THE LAWS OF GREAT BRITAIN, OF 36 HYDE ROAD, DENTON, MANCHESTER, LANCASHIRE, ENGLAND.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed:—

This invention relates to electric secondary cell containers and more particularly to containers for traction cells. The invention also relates to electric batteries and cells including such containers.

In the past electric batteries made up of a number of individual cells have been separated from one another within the battery casing by wood packing pieces which maintain spaces between the cells through which cooling air may circulate. The use of separate wood packing pieces in this way tends to be expensive and has the disadvantage that the wood shrinks leaving the cells free to move in the casing with the possibility of damage to the components if the battery is used in arduous conditions of the kind which are commonly experienced in mines.

It is an object of the present invention to provide an electric secondary cell container which may be used in an electric battery to provide at least the same spaces for the circulation of cooling air as are provided by wood packing pieces, but which avoids the disadvantages attendant upon the use of wood packing pieces.

According to the present invention there is provided an electric secondary cell container on the outside of the walls of which are formed spacing ribs which extend beyond the base of the container so that, when a plurality of containers are placed in juxtaposition in a casing, channels are formed for air to circulate under and between the containers.

Preferably the tops of the spacing ribs are below the top of the container.

According to one aspect of the invention there is provided an electric secondary cell container having on the outside walls thereof spacing ribs the tops of which are below the top of the container, and which ribs extend beyond the base of the container, the container and the ribs being moulded in hard rubber and the ribs being arranged such that, when a plurality of containers are placed in juxtaposition in a casing, channels are formed for air to circulate under and between the containers.

According to another aspect of the invention there is provided an electric battery comprising an outer casing, a plurality of secondary cells in the casing, characterised by each cell being housed in a container on the outside walls of which container there are provided moulded spacing ribs which extend beyond the base of the container and which are arranged such that cooling air may circulate between the individual cells and between the cells and the casing.

The invention will be better understood from the following detailed description of one embodiment thereof which is shown by way of example in the accompanying drawings. In the drawings :—

Figure 1 is a part sectional plan view of a secondary cell having a container according to the invention,

Figure 2 is a diagrammatic plan view of a portion of an electric battery showing a casing containing twenty-four cells having containers according to the invention and half an adjoining casing, and

Figure 3 is a diagrammatic front elevation of the portion of the electric battery shown in Figure 2 with the front of the casing and the insulator at the front removed.

Referring to the accompanying drawings there is shown a cell 1 in the container 2 of hard rubber. Moulded integrally with the container 2 are spacing ribs 3 and 4. These ribs 3 and 4 extend beyond the base 5 of the container, as shown in Figure 3. At the centre of the base 5 there is provided a moulded projection 6 of the same length as the extensions beyond the base 5 of the container of the ribs 3 and 4. The projection 6 is also moulded integrally with the container 2.

In Figures 2 and 3 there is shown a portion of an electric battery in which the cells 1 are assembled within a sheet steel casing 7 on the inside of which there is an ebonite liner 8. The spacing ribs 3 and 4 on adjacent cells but together leaving substantial spaces or channels 9 and 10 between the cells 1 through which cooling air may circulate. On the cells nearest the casing 7 these ribs 3 and 4 form air channels between the cells and the ebonite liner 8 on the casing 7. Also the extensions of the ribs 3 and 4 below the base of the containers 2 of the cells 1 leave a channel 11 between the cells and the ebonite liner 8 on the base of the casing 7 so that cooling air may circulate beneath the cells 1.

Referring to Figure 3 it is shown that the tops of the spacing ribs 3 and 4 stop short of the top of the cell.

In the embodiment of the invention shown in Figure 3, the height of the cell is approximately 17 inches while the portion of the ribs 3 and 4 extending beneathe the cell is $\frac{1}{4}$ inch and the tops of the ribs 3 and 4 stop about $\frac{1}{2}$ inch from the top of the cell container.

The fact that the ribs 3 and 4 stop short of the top of the cell container results in a long electrical tracking path between the terminals of adjacent cells 1. This long tracking path is more efficient than a similar-lengthed tracking path previously obtained with separate wood packings, as the wood was liable to absorb moisture of spilt electrolyte and was not as efficient an insulator as the hard rubber ribs. Similarly an effective long tracking path is obtained between the outer cells 1 and the sheet steel casing 7.

In the embodiment of the invention which has been described the container 1 has three ribs on two of its sides and two ribs on the other two sides. The numbers of ribs on the various sides of the container may be varied, however, according to the particular purpose for which the cell is designed, for example if greater stiffness is required three ribs may be provided on each of the sides. When there are three ribs on any side of the container, it is preferred that the middle rib shall not extend beyond the base of the container.

Price : TWO RUPEES

By means of the present invention a greater mechanical strength is imparted to each cell, and wood packings can be dispensed with while adequate cell ventilation is still provided.

WE CLAIM :—

1. An electric secondary cell container on the outside walls of which are formed spacing ribs which extend beyond the base of the container, so that, when a plurality of containers are placed in juxtaposition in a casing, channels are formed for air to circulate under and between the containers.

2. A container according to Claim 1 in which the tops of the spacing ribs are below the top of the container.

3. An electric secondary cell container having on the outside walls thereof spacing ribs the tops of which are below the top of the container, and which ribs extend beyond the base of the container the container, and the ribs being moulded in hard rubber and the ribs being arranged such that, when a plurality of containers are placed in juxtaposition in a casing, channels are formed for air to circulate under and between the containers.

4. An electric secondary cell container substantially as described with reference to the accompanying drawings.

5. An electric secondary cell having a container according to any one of the preceding claims.

6. An electric battery comprising an outer casing, a plurality of secondary cells in the casing, characterised by each cell being housed in a container on the outside walls of which container there are provided moulded spacing ribs which extend beyond the base of the container and which are arranged such that cooling air may circulate between the individual cells and between the cells and the casing.

7. An electric battery substantially as described with reference to the accompanying drawings.

B. DePENNING

of DePENNING & DePENNING.

Agents for the Applicants.

Dated this 22nd day of December 1960.

Printed by The Nelys Printing Works, Calcutta-1.

FIG. 1

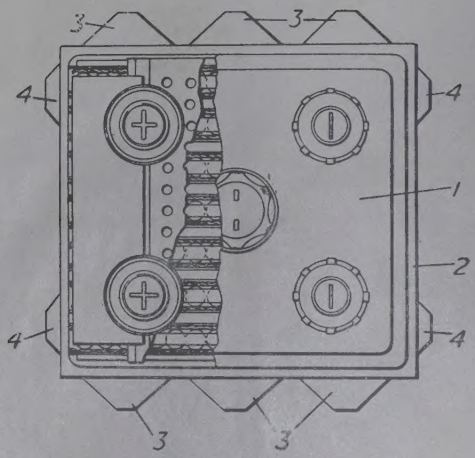

FIG. 3.

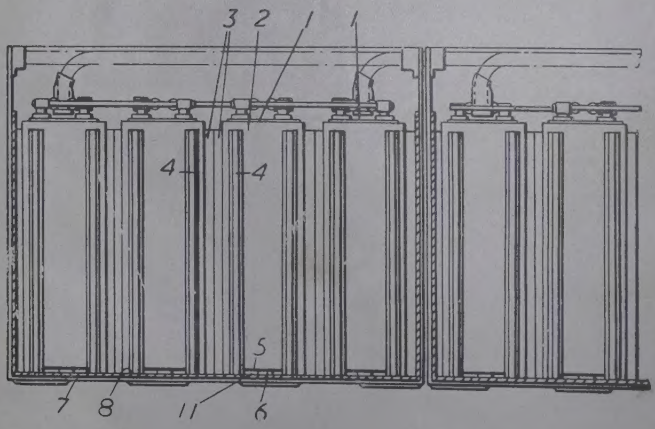

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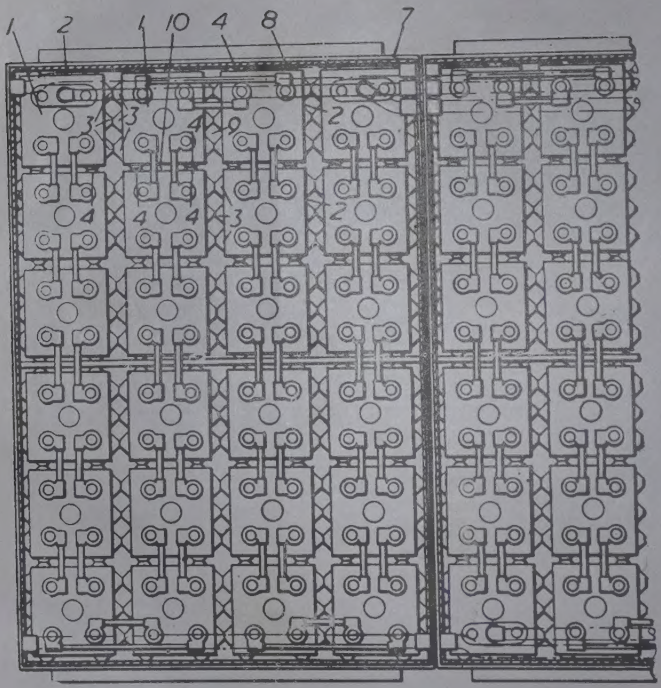
FIG. 2



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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17

Specification No. 74639. Application No. 74639, dated 22nd December 1960. Complete Specification left on 14th March 1961. (Application accepted 11th January 1961.)

PROVISIONAL SPECIFICATION

(Section 4)

" IMPROVEMENTS IN OR RELATING TO TAPE DISPENSERS. "

AMAR INDUSTRIES, an Indian Firm, of 6, Kermani Building, Sir Phirozshah Mehta Road, Fort, Bombay 1, the State of Maharashtra, India.

The following Specification describes the nature of this Invention :—

This invention relates to a tape dispenser; more particularly, this invention relates to a tape dispenser of the kind used for dispensing requjred lengths of an adhesive tape from a roll of the said tape held in the dispenser.

This invention has for its object an automatic tape dispenser which will enable the tape to be applied to any surface merely by moving the said dispenser on the desired length of the surface to which the tape should be applied.

With this object in view, the improved tape dispenser according to this invention consists of a gadged which has in combination (i) a container for the adhesive tape, (ii) a roller adapted to press the released tape automatically and continuously on the surface to which the said tape should be applied, and (iii) a blade or like cutting device which is built in with the body of the dispenser for separating the attached portion of the tape from the main stock of the tape.

This invention will now be more particularly described with reference to the accompanying drawing which is a perspective view of one embodiment of an improved tape dispenser according to this invention, it is to be understood, however, that the dispenser illustrated in the drawing will be described merely by way of an example and not by way of any limitation of this invention.

The tape dispenser illustrated in the drawing has for its essential parts:- a container 1, a rubber roller 2 and a metallic cutting blade 3.

The container 1 is adapted to hold a roll 4 of the adhesive tape, and it may be provided with a lid for closing it.

The roller 2 is made of rubber or like resilient material and it is built in at the tape delivery end of the container in such a manner as to press upon the unwound portion 5 of the tape fed through a slit 6 provided at the side of the said roller 2.

As the roller is moved on the surface to which the tape should be attached, the tape roll 4 will be automatically unwound and the unwound portion 5 will be automatically pressed against the said surface.

When the desired length of the tape has been released and automatically pasted, the cutting blade 3 built in on the container 1, a little in front above the roller 2, will be pressed down to cut away the pasted portion of the tape from the main stock of the tape in the roll 4 held in the container 1.

Thus the said tape dispenser will function as an automatic dispenser in which, after once the tape has been fed inside and one end of it has been released through the slit provided thereon, there will be no necessity of touching the tape again for the purpose of pressing it on the surface; moreover, the tape delivered from the said dispenser will straight away be applied on to the surface merely by moving the dispenser on the desired length of the surface to which the tape should be attached.

After the desired length of the tape has been attached to the surface, the dispenser can just be pressed forward, whereupon the tape will be cut and severed at the desired spot by means of the metallic blade 3 provided at the release end of the dispenser.

When the tape is to be applied again to the surface, it will only be necessary to bring the cut-end of the tape in the dispenser into contact with the surface and again move on the gadget continuonsly along the said surface until the required length of the tape is again applied to the surface.

B. DePENNING
of DePENNING & DePENNING
Agent for the Applicants.

Dated this 22nd day of December 1960.

COMPLETE SPECIFICATION

(Section 4)

Specification No. 74639.

" IMPROVEMENTS IN OR RELATING TO TAPE DISPENSERS. "

AMAR INDUSTRIES, an Indian Firm, of 6, Kermani Building, Sir Phirozshah Mehta Road, Fort, Bombay 1, the State of Maharashtra, India.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :-

This invention relates to a tape dispenser; more particularly, this invention relates to a tape dispenser of the kind used for dispensing required lengths of an adhesive tape from a roll of the said tape held in the dispenser.

This invention has for its object an automatic tape dispenser which will enable the tape to be applied to any surface merely by moving the said dispenser on the desired length of the surface to which the tape should be applied.

Price : TWO RUPEES.

With this object in view, the improved tape dispenser according to this invention consists of a gadget which has in combination (i) a container for the adhesive tape, (ii) a roller adapted to press the released tape automatically and continuously on the surface to which the said tape should be applied, and (iii) a blade or like cutting device which is built in with the body of the dispenser for separating the attached portion of the tape from the main stock of the tape.

This invention will now be more fully described with reference to the drawings accompanying the Complete Specification, in which :-

Fig. 1 shows the lid of a tape dispenser according to this invention.

Fig. 2 shows a roll of adhesive tape for use in the said tape dispenser.

Fig. 3 shows the said dispenser with its lid removed.

Fig. 4 shows how the tape is released from the dispenser.

Fig. 5 shows the disposition of the cutting blade in relation to the tape released from dispenser.

Fig. 6 is a section on A-A of Fig. 5.

Fig. 7 shows the initial application of the tape released from the said dispenser, for joining two surfaces together.

Fig. 8 shows the same at a more advanced stage of the application.

Fig. 9 shows the position for severing the tape from the applied surface.

Fig. 10 shows the finished joined surface.

The tape dispenser illustrated in the drawings is made in two parts comprising a container 1 and a lid 2 for the said container.

On the container 1 and integral therewith is provided an annular tape roll holder 3 on which a roll 4 of adhesive tape may be loosely loaded. The container 1 is also provided with a stud 5 whereby a roller of spongy rubber 6 may be fitted on the dispenser at the delivery end thereof.

The lid 2 is fitted with a flange 7 which will bear against wall of the container 1, and with a socket 9 into which the stud 5 will fit when the lid 2 is fitted on the container 1. It is also provided with a circular opening 10 having a rim 11 adapted to fit into the annular holder 3.

On the stud 5 is fitted the spongy rubber roller 6, leaving a gap 12 between the said roller 6 and the wall 8 of the container on one side of the roller.

On the said wall 8, on the opposite said in relation to the gap 12, is built in a cutter blade 13, a little in advance of the said roller 6.

The tape dispenser illustrated in the drawing is used as follows:-

To start with, the tape roll 4 is loaded on the tape roll holder 3, and the tape 14 is drawn off from the said roll 4 until its free end 15 extends outside through the gap 12.

The container 1 is then fitted with the lid 2 so that the flange 7 bears against the wall 8, the rim 11 fits into the tape roll holder 3 and the stud 5 fits into the socket 9. Thus the said container and its lid will form a single unit for operation.

For using the tape loaded dispenser, e.g. for joining together tow pieces 16 and 17 of a slip of paper torn along the line 18, the said pieces are kept side by side with each other, with the line 18 common to both, and the tape end 15 is pressed by means of the roller 6 so as to cover the said pieces 16 and 17 at one end of the said line 18, as shown in Fig. 7.

As soon as the said pieces are adhered together at the said end of line 18, the dispenser is gradually moved along the said line 18 (as shown in 18) towards the opposite end of the line 18, with the roller continuously pressed on the tape 14 which will be released the through gap 12.

As soon as the roller 6 has moved to the said opposite end of the line 18, the dispenser is tilted slightly so that the adhesive tape comes into contact with the blade 13 and it is then severed from the applied surface as shown in Fig. 9.

When the tape dispenser has to be used again, it will only be necessary to bring the cut-end of the tape in the dispenser into contact with the surfaces to be joined together and to roll it continuously along the joining line of the said surfaces until the required length of the tape is again applied to the said surfaces.

Thus, the improved tape dispensor according to this invention is automatic in its operation; that is to say, once the tape is loaded into the dispenser and its end is taken out through the slit, the need for touching the tape with the hand is altogether dispensed with; the pasting of the tape one the desired surface will be done automatically by the roller, such a modus operandi provides a great convenience, as it affords to the operator of the tape dispenser, the great advantage that his hands and fingers need not be soiled or dirtied by the adhesive during the affixing operation.

It is to be understood that the dispenser illustrated in the drawing has been described merly by way of an example and not by way of any limitation of this invention and its design and details may be varied without departing from the spirit of this invention.

WE CLAIM :—

1. An improved tape dispenser which consists of a gadget which has in combination (i) a container for the adhesive tape, (ii) a roller adapted to press the released tape automatically and continuously on the surface to which the said tape should be applied, and (iii) a blade or like cutting device which is built in with the body of the dispenser for separating the attached portion of the tape from the main stock of the tape.

2. An improved tape dispenser according to Claim 1, in which the said roller is made of rubber or like resilient material.

3. An improved tape dispenser according to Claim 1 or 2, in which the said roller is built in at the tape delivery end of the container for the adhesive tape, in such a manner as to be capable of being pressed upon the unwound portion of the tape fed through a slit provided by the side of the said roller.

4. An improved tape dispenser substantially as described and illustrated.

B. DePENNING
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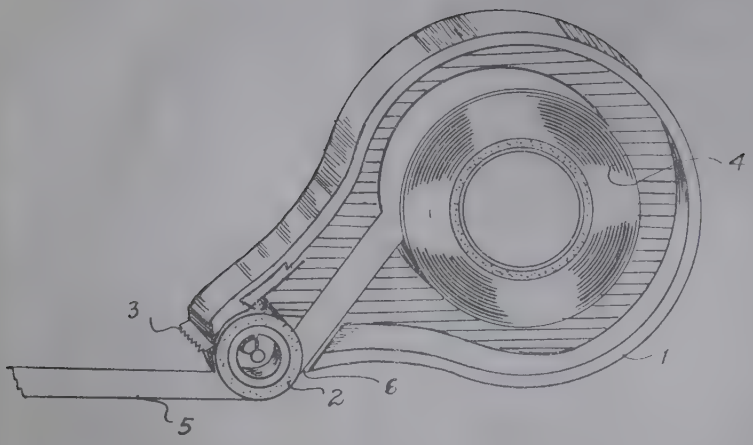
Agent for the Applicants.

Dated this 14th day of March 1951.

Printed by The Nelys Printing Works, Calcutta-1.

Amar Industries. Provisional Specification. One Sheet.

No. 74639.



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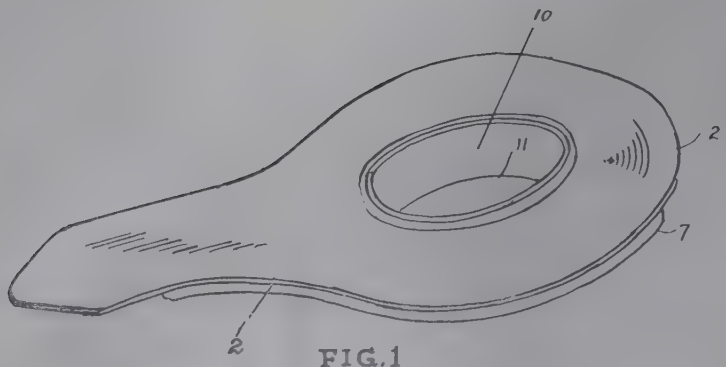

FIG.1

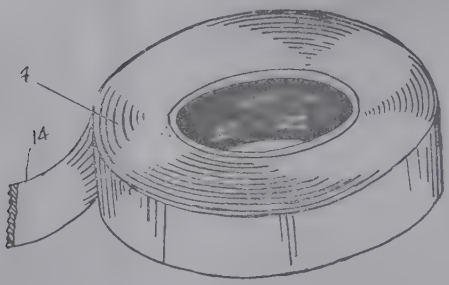

FIG.2

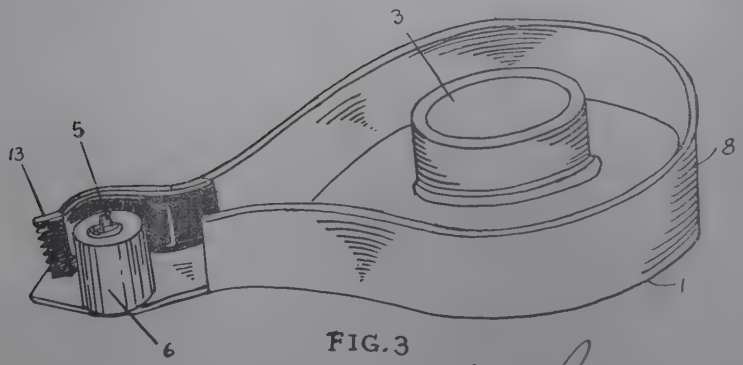

FIG.3

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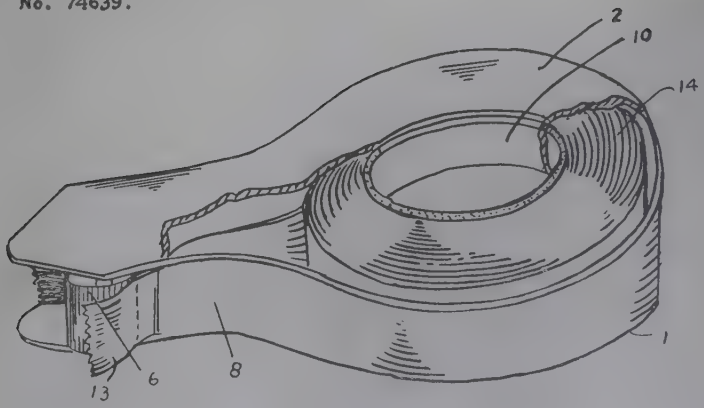

FIG. 4

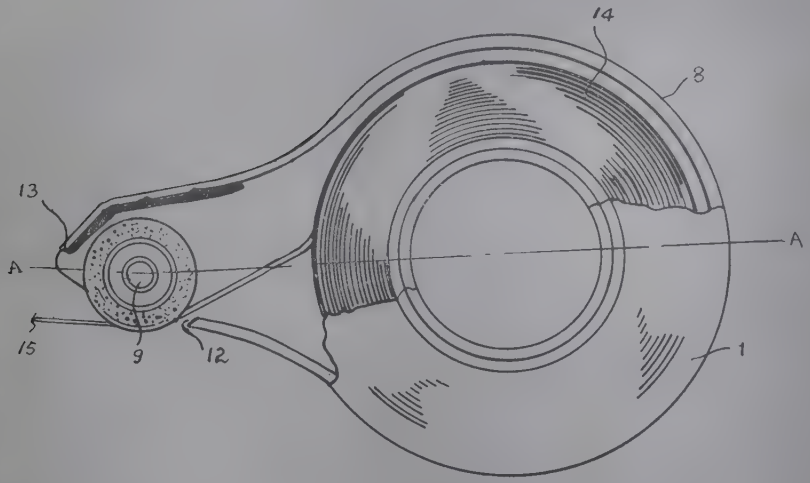

FIG. 5

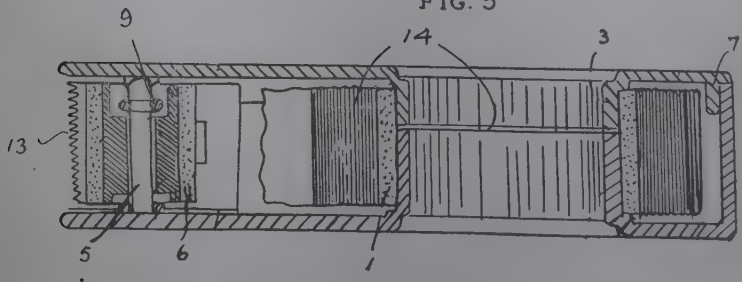

FIG 6

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Agent for the Applicants.

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.
Specification No. 74641, filed 22nd December 1960./1 Paus 1882 (Saka).
(Accepted 18th January 1962).

" SLIDE FASTENERS. "

TADAO YOSHIDA, of 339, Suwadacho-2-chome, Ichikawa-shi, Japan, of Japanese Nationality.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

The presnt invention relates to slide fasteners and particularly those having a pair of generally helically coiled interlocking elements, and has for its object to provide a new and improved slide fastener having such interlocking elements of unique configuration effective to ensure firm and positive interlocking while enabling the interlocking elements to be held securely in place on respective carrying tapes or strips.

Another object of the present invention is to provide an improved slide fastener of the kind described of which interlocking elements are substantially free from cracking or breakage even under considerably severe bending and/or other physical stresses.

A further object of the present invention is to provide an improved slide fastener of the kind described which is extremely simple and economical to manufacture as compared with any previous slide fasteners having interlocking means of the same general kind.

A still another object of the present invention is to provide an improved slide fastener of the kind described in which a slide member may be arranged, in assemblying the slide fastner, so as to operate to effect interlocking of the slide fastener while sliding in either of opposite directions longitudinal of the slide fastner as desired.

According to the present invention, there is provided a slide fastener comprising a pair of generally helically coiled interlocking elements formed of flexible and resilient metal or synthetic resin wire bent into two rows of spaced U-formations lying in transversely spaced parallel planes, one for each row, said U-formations in one of said rows each having legs connected at the extremities thereof with those of transversely aligned legs of adjacent respective U-formations in the other row by transversely extending bridge portions of the wire, said bridge portions being each laterally enlarged to form an intlocking tooth including lateral porjections symmetrically shaped with respect to the plane containing said bridge portion and the associated transversely aligned legs, and further comprising a pair of carrying strips one for each of said interlocking elements each fitted along one of side edges thereof in between said two rows of U-formations of the associated interlocking element, and a pair of holding strips of limited width integrally secured to each of said carrying strips on opposite sides thereof with the rows of U-formations of the associated interlocking element interposed between the carrying strip and the respective holding strip so as to be covered substantially entirely excepting those portions of the U-formations which are close to the respective bridge portions.

The present invention will now be described in detail in connection with the accompanying drawings which illustrate one embodiment of the invention. In the drawings :

Fig. 1 is a front view of a slide fastener embodying the present invention;

Fig. 2 is a sectional view substantially taken along the the line B-B in Fig. 1, looking in the direction indicated by the arrows;

Fig. 3 is a front view of one of the interlocking elements;

Fig. 4 is a sectional view of same substantially taken along the line A-A in Fig. 3, looking in the direction indicated by the arrows;

Fig. 5 is a side view of the interlocking element shown in Fig. 3, as viewed from the left-hand side as appearing in Fig. 3; and

Fig. 6 is a front view of a pair of such interlocking elements in interlocking relation to each other.

In the drawings, there is shown a slide fastener which comprises a pair of generally helically coiled interlocking elements 1 formed of flexible and resilient metal or synthetic resin wire bent into two rows of spaced U-formations lying in transversely spaced parallel planes, one for each row, each of the U-formations in one of said rows having legs 1′ connected at the extermities thereof with those of transversely aligned legs of adjacent respective U-formations in the other row by transversely extending bridge portions of the wire, as shown. It will be observed that the transversely extenping bridge portions are each laterally enlarged to form an interlocking tooth including lateral projections 1″ symmetrically shaped with respect to the plane containing the bridge portion and the associated transversely aligned legs.

The slide fastener also comprises carrying tapes or strips 6, one for each interlocking element 1, which are each fitted along one of its side edges in between the two rows of U-formations of the associated interlocking element 1. Further, a pair of holding tapes or strips 2 of limited width are provided for each of the carrying tapes 6 and integrally secured thereto on opposite sides thereof with the rows of U-formations of the associated interlocking element interposed between the carrying strip 6 and the respective holding strips 2 in a manner so that the U-formations are covered substantially entirely by the respective holding strips 2 with the exception of those portions of the formations which are close to the respective bridge portions and thus seburely held in place on the carrying tape 6. It is to be noted that the holding strips 2 are provided not only for collateral or auxiliary purposes as is the case with conventional slide fasteners but also function as a guide for sliding movement of a slider member 5 for operating the slide fastener while protecting the interlocking elements 1 from impacts or other exterior physical stresses by covering the elements 1 substantially entirely. It will be appreciated that the symmertical shaping of all the interlocking teeth of each of the interlocking elements 1 as described hereinabove makes it possible, in assembling the slide fastener, to arrange the slider member 5 relative to the interlocking elements so as to be operated in either of opposite directions longitudinal of the slide fastener as desired to bring the pair of interlocking elements into interlocking relation to each other.

It will further be appreciated that the interlocking elements of the slide fastener according to the present invention can be firmly interconnected with each other by the operation of the slide member because of their special configuration as described above while being each securely held in the place on the carrying strip by the holding tapes secured thereto.

As a further characteristic feature of the present invention, it will also be appreciated that, as distinct from previous slide fasteners having generally helically coiled interlocking elements which are likely to be broken or cracked as when subjected to bending, the interlocking elements according to the present invention are substantially free from such cracking or breakage even under considerably severe bending and/or other external physical stresses.

It should also be recognized that the slide fastener of the present invention is extremely simplified and economical to manufacture as compared with any conventional slide fasteners having generally helically coiled interlocking elements.

I CLAIM :—

A slide fastener comprising a pair of generally helically coiled interlocking elements formed of flexible and resilient metal or synthetic resin wire bent into two rows of spaced U-formations lying in transversely spaced parallel planes, one for each row, said U-formations in one of said rows each having legs connected at the extremities thereof with those of transversely aligned legs of adjacent respective U-formations in the other row by transversely extending bridge portions of the wire, said bridge portions being each laterally enlarged to form an interlocking tooth including lateral projections symmetrically shaped with respect to the plane containing said bridge portion and the associated transversely aligned legs, and further comprising a pair of carrying strips one for each of said interlocking elements each fitted along ond of side edges thereof in between said two rows of U-formations of the associatd interlocking element, and a pair of holding strips of limited width integrally secured to each of said carrying strips on opposite sides thereof with the rows of U-formations of the associated interlocking element interposed between the carrying strip and the respective holding strips so as to be covered substantially entirely excepting those portions of the U-formations which are close to the respective bridge portions.

B. DePENNING
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Agent for the Applicant.

Dated this 22nd day of December 1960.

Printed by The Nolys Printing Works, Calcutta-1.

T. Yoshida.
NO. 74641.

One Sheet.

Fig. 1.

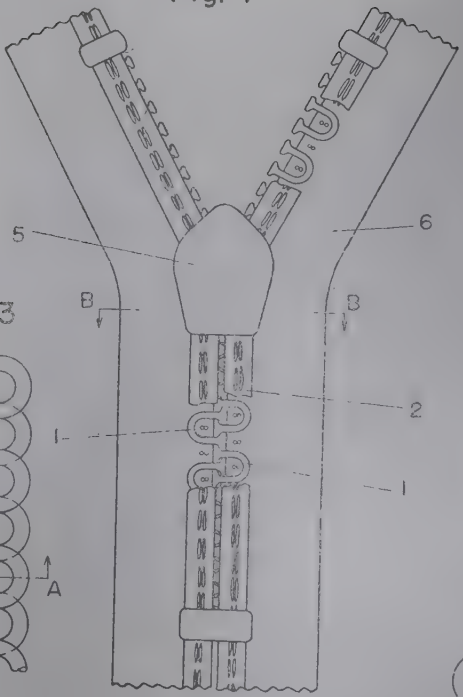


Fig. 5

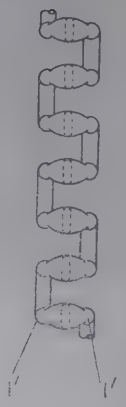


Fig. 3

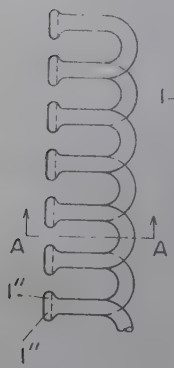
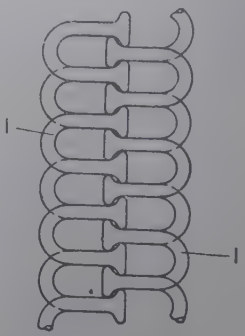


Fig. 6



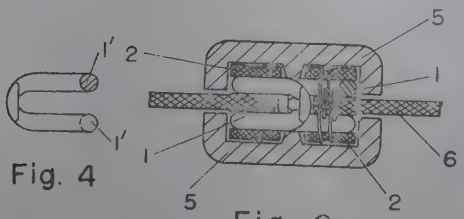


Fig. 4

Fig. 2

B. DePenning

of DePENNING & DePENNING
Agent for the Applicant.

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74642, filed 22nd December 1960./1 Paus 1882 (Saka.) (Accepted 7th May 1962.)

STABILIZED FORMALDEHYDE POLYMERS AND METHOD FOR PREPARING THEM.

SOCIETA ITALIANA RESINE, an Italian Joint Stock Company, of 33, Via Grazioli, Milan, Italy.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention concerns stabilization of high polymers of formaldehyde by means of chemical reactions involving the terminal groups of the molecules of the polymers.

It is known that high polymers of formaldehyde can be thermally and chemically stabilized by esterification or etherification of the terminal hydroxyl groups (R. Staudinger "Die hochmolekularen organischen Verbindungen" Springer/Berlin, 1932 page 230 and following pages, and J. F. Walker "Formaldehyde", Reinhold Publ. Corp./New York, 1953 page 138 and following pages).

The yield of the known processes is relatively low unless a large proportion of esterifying or etherifying agent is employed, part of the polymer undergoing in any case a degradation.

It has now been found that high polymers of formaldehyde can be satisfactorily stabilized in an easy, safe and inexpensive manner by converting their terminal hydroxyl groups to esters of carbamic acids through reaction with alkyl- or aryl mono isocyanates whether in the presence of catalysts or not.

The resulting products exhibit at 222°C a thermal degradation ratio lower than 1% per minute. Infrared ray analysis of the polymer stabilized as indicated above does not disclose any trace of free hydroxyl groups.

The method is carried out broadly as follows.

The high polymer of formaldehyde is suspended in a thoroughly anhydrous inert liquid medium, (such as an aromatic or aliphatic hydrocarbon), in which the isocyanate selected for stabilization is dissolved; the reaction temperature can vary within a wide range according to the properties of the isocyanates and reaction medium.

For activating the stabilizing reaction catalysts can be employed which catalyse the formation of carbamic groups, such as tertiary aliphatic or aromatic amines, arylphosphines and alkylphosphines.

The reaction temperatures and time mainly depend upon the activity of the isocyanate employed. The process is generally carried out between 15° and 70°C during a time of 20 minutes to a few hours. Reflux is normally resorted to whereby the highest temperature is the boiling temperature of the inert liquid in which the stabilizing reaction is effected.

Among isocyanates which can be used for the purpose in view phenylisocyanate and paratoluenisocyanate are preferred, while tri-n-butylamine or triphenylphosphine can be used as catalyst.

The following examples will explain the invention without, however, limiting the same.

Example 1

240 grams polyformaldehyde of high molecular weight in a finely subdivided condition (viscosity of a 0·5% solution in p-chlorophenol admixed with 2% alphapinene = 2·0 calculated as $\frac{\eta \text{ Solution} - 1}{\eta \text{ Solvent}} \cdot \frac{1}{C}$) are suspended in one liter anhydrous n-heptane in a 5 liter-flask provided with a stirrer, a funnel with a cock and a condenser connected to a magnesium perchlorate drying column. While stirring the solution is heated to 35°C and 2 grams freshly distilled phenyl-isocyanate dissolved in 300 cbc n heptane are supplied during 30 minutes, whereupon stirring is pursued at 35°C during a further hour. Upon cooling the stabilized polymer is filtered, washed with hot methanol and dried at 40°C in an oven at a reduced pressure. The resulting polymer is actually unchanged in viscosity, its constant of thermal stability being 0·05% per minute at 222°C ascertained by the method of M. A. Naylor and A. W. Anderson, J. Am. Chem. Soc. 76, 3962 (1954).

Example 2

700 cbc freshly distilled anhydrous n-heptane containing 0·07 grams tri-n-butylamine are poured into a 3 liter-flask provided with a stirrer, a funnel with a cock and condenser with a dehydrating trap. 120 grams polyformaldehyde of high molecular weight (viscosity 3·86) in a finely subdivided condition are introduced while vigorously stirring. The suspension is heated to 50°C and admixed during one hour with a solution of 1·4 grams p-toluen-isocyanate dissolved in 350 cbc anhydrous n-heptane. The reaction is pursued during further two and a half hours. Upon filtering, the stabilized polymer is washed with hot methanol and dried in an oven at 40°C at a reduced pressure. Its viscosity amounts to 3·85, its thermal stability constant being 0·02% per minute at 222°C. The viscosity and thermal stability constant are determined as indicated in Example 1.

Example 3

120 grams polyformaldehyde of high molecular weight in a finely pulverised condition (viscosity = 2·7 measured as indicated in Example 1) are suspended in 500 cbc benzine (petrol) in a flask identical to that of Example 2 (the distillation curve of the benzine being between 80° and 120°C). While further stirring 0·12 grams triphenylphosphine dissolved in 200 cbc of benzine are added at room temperature. The reaction mixture is heated to 60°C and admixed during 15 minutes with 0·9 grams phenylisocyanate dissolved in 100 cbc of benzine. Stirring is pursued during 45 minutes. Upon filtering the stabilized polymer is washed with hot methanol and dried at 45°C at a reduced pressure. Its viscosity is unchanged with respect to the starting polymer, its heat stability constant being 0·04% per minute.

The polymers prepared according to the above examples disclose at infrared analysis a practically total freedom from hydroxyl groups which are clearly detectable under same conditions in the unstabilized starting polymer.

We claim:

1. Process for stabilizing formaldehyde polymers of high molecular weight, comprising coverting the terminal hydroxyl groups of the polymer to carbamates by reacting the polymer suspended in an anhydrous inert solvent with a member selected from the group consisting of alkyl- and arylmonoisocyanates.

2. Process as claimed in Claim 1, wherein a catalyst is employed selected from the group consisting of tertiary aliphatic and aromatic amines, arylphosphines and alkylphosphines.

3. Process as claimed in Claim 1, wherein the said member consists of paratoluenisocyanate.

4. Process as claimed in Claim 1, wherein the said member consists of phenylisocyanate.

5. Process as claimed in Claim 1, wherein tri-n-butylamine is employed as a catalyst.

6. Process as claimed in Claim 1, wherein triphenylphosphine is employed as a catalyst.

7. Process as claimed in Claim 1, wherein the solvent is selected from the group consisting of aliphatic and aromatic liquid hydrocarbons.

B. DaPENNING,

or DaPENNING & DaPENNING.

Agent for the Applicants.

Dated this 22nd day of December 1960.

Price : TWO RUPEES.

MGIP Santh.—SL—38 Patent 62—18-3-63—100.

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74643. Application No. 74643, dated 22nd December 1960. Complete Specification left on 24th October 1961. Addition No. 60304. (Application accepted 4th April 1962.)

PROVISIONAL SPECIFICATION.

AN IMPROVED FIBRE-CARDING AND DRAFTING MACHINE.

SHRIDHAR RAMCHANDRA SATHE, INDIAN SUBJECT, PROPRIETOR : TILAK SANSHODHAN MANDIR, 418-A, NARAYAN PETH, POONA-2, INDIA

The following specification describes the nature of this invention.

This invention relates to the improvements made in or relating to the Fibre-Carding and Drafting Machine which is the subject matter of the invention patented under No. 60304, on the 25th April, 1957, in the name of the present applicant.

The improvements effected in the patented invention are briefly described as under :

(1) The changing of motion of the collecting and drawing rollers by gears on the same shafts, but by shifting the chain from one to the other, is provided for.

(2) The introduction of the central pressure system (by one single spring each side) on the drawing rollers gives easy and nice effect of pressure on the roller.

(3) Sliver collection in the rotating tin by means of a ring moving up and down effects better binding of the same.

(4) A combed cotton feed plate at the edge increases the output and at the same time lessens the driving pressure and breakage of fibres, and better opening of the naps is effected. This invention will improve the quality of the slivers and consequently the quality of the yarn.

(5) Provision of the brushes at the side of the lickerin roller prevents collection of fibres at the sides of the shaft. This will avoid frequent cleaning and also friction caused by the collection of fibres between the shaft and the bearings.

M. P. SHIKHARE.

Attorney for and on behalf of the Applicant.

Dated this 21st day of December 1960.

COMPLETE SPECIFICATION.

SHRIDHAR RAMCHANDRA SATHE, INDIAN SUBJECT, PROPRIETOR : TILAK SANSHODHAN MANDIR, 418-A, NARAYAN PETH, POONA-2, INDIA.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to the improvements made in or relating to the automatic fibre-equalising machine, patented under No. 60304, on the 25th April 1957, in the name of the present Applicant.

According to this invention, the improved fibre-carding and drafting machine having a feed plate is provided with a comb at the feeding point, brushes at the sides of the likerin and a spring at each end over a common plate on the top of the drafting rollers.

This invention is illustrated in the accompanying drawing throughout which like reference figures indicate corresponding parts. In this drawing the perspective view is shown.

The cotton feed plate 1 is provided with a comb 2 at the feed point. Thereby cotton fibres are opened in a better manner. This further reduces the driving load and fibre-breakage. Brushes 3 are secured at the sides of the likerin 4. This addition of brushes prevents the collection of cotton fluff near the bearings 15 of the likerin shaft and avoids its frequent jamming. Spring 9 is loaded at each end over a common plate 11 resting over the bearings of the top rollers 6 and 10. Bolt 12 which is secured on the framing 13 passes through plate 11 and spring 9. Fly nut 14 controls the pressure of spring 9. Similar arrangement is made on the off side of the top rollers 6 and 10 as shown. Spring 9 exerts pressure uniformly on both the rollers 6 and 10.

I claim :

1. An improved fibre-carding and drafting machine having a feed plate with a comb at the feeding point, brushes at the sides of the likerin and a spring at each end over a common plate on the top of the drafting rollers.

2. An improved fibre-carding and drafting machine, according to Claim 1 substantially as described and illustrated.

M. P. SHIKHARE.

Attorney for and on behalf of the Applicant.

Dated this 20th day of October 1961.

Price : TWO RUPEES.

MGIP Sauth—SL—34 Patent/62—5-3-63—100.

No. 74643 OF 1961. No. OF SHEETS. 1.

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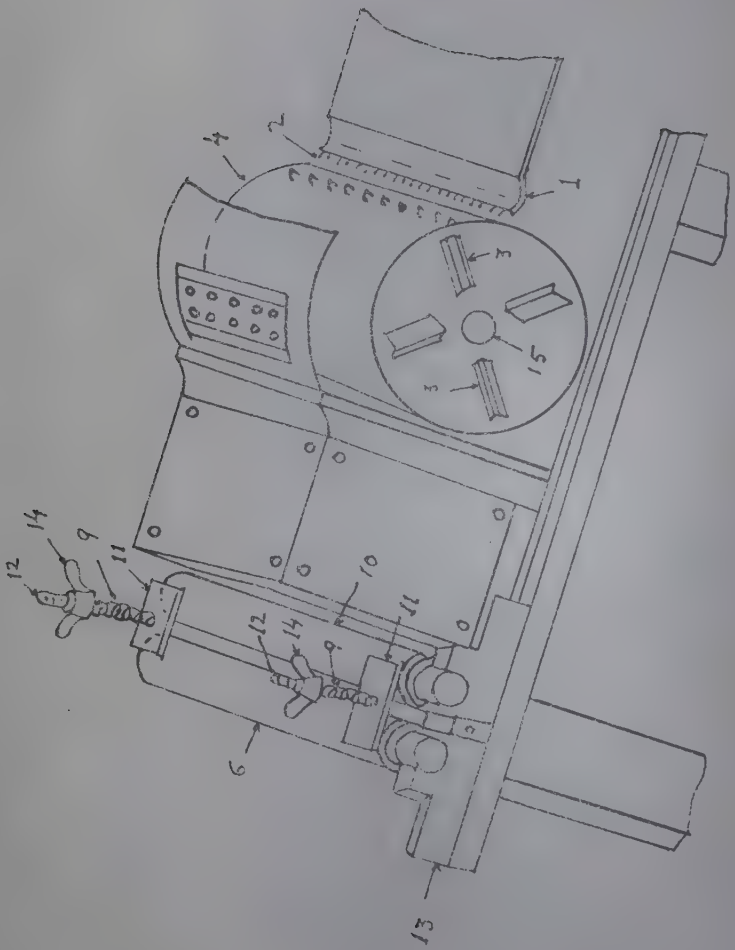
SATHE. SHEET NO. 1.



S. R. Sathe

REG. NO. 2073 1-44 10672

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74644. Application No. 74644, dated 22nd December 1960. (Addition to No. 61888.) Complete specification left 24th October 1961. (Application Accepted 4th April 1962.)

IMPROVED HAND SPINNING WHEEL, I. E., CHARKHA

PROVISIONAL SPECIFICATION.

SHRIDHAR RAMCHANDRA SATHE, Indian Subject, 418-A, Narayan Peth, Poona-2, India.

The following specification describes the nature of this invention.

This invention relates to the improvements made in or relating to the Hand Spinning Wheel which is the subject matter of the invention patented under No. 61888, on the 28th September 1957, in the name of the present applicant.

(1) In this invention the number of the gears is minimised with the help of one neutral gear and one gear fixed on the front roller shaft. These and other gears are very easy to fix and remove, and the changing of gears to change the draft is effected in a very easy manner.

(2) The main drive gear is fixed on the same plate and the fixing bolt of the plate also serves the purpose of the axle of the main gear. This facilitates the tightening of the front driven shaft without affecting the rest of the transmission system. This invention eliminates the belt-tightening pulley.

(3) In this invention the changing of distance between the couples of drafting rollers is effected easily and also made sensitive by means of the top bearings plate of the same connected with each other by means of a bolt and a nut and the top roller-pressure system being individual and cumulative. This has made the adjustment of pressure easier.

(4) A sliding channel provided between the drafting rollers helps to increase cohesion and accumulation of fibres. It saves the fall-down of short fibres and avoids suspension of the same in the yarn.

(5) In this invention taper package winding by central pull to the ring plate by heart cam and ratchet, gear, is provided for.

M. P. SHIKHARE.

Attorney for and on behalf of the Applicant.

Dated this 21st day of December 1960.

COMPLETE SPECIFICATION.

SHRIDHAR RAMCHANDRA SATHE, Indian Subject, PROPRIETOR : TILAK SANSHODHAN MANDIR, 418-A, Narayan Peth, Poona-2, India.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to the improvements made in or relating to the Hand Spinning Wheel, i.e., Charkha, patented under No. 61888, dated 28th September 1957, in the name of the present Applicant.

The improvements effected in the aforesaid patent are as follows :

Hithertobefore the top drawing rollers were supported in open bearings. They are now supported by adjustable and swivelling bearing plates from the top with tension springs on them;

Sliding channel plates are newly introduced between each pair of drawing rollers;

Taper package building mechanism is newly introduced for winding yarn on bobbins;

Chain drive system for driving the drawing rollers is replaced by gear drive mechanism;

This invention is illustrated in the accompanying drawings throughout which like reference figures indicate corresponding parts. In these drawings Fig. A is the perspective view of the invention; Figs. B and D show the adjustable swivelling bearing plates to cover the top rollers and Fig. C shows the sliding channel plates between the pairs of drawing rollers.

In Fig. A, hand wheel 1 drives the front roller pinion 2 which is in turn secured to the front roller shaft 3. Hand wheel 1 has a handle 4 secured on it. Hand wheel 1 freely rotates on stud 5 which is secured in slot 7 of the framing 8. Slot 7 facilitates adjustments in gear wheels for any change of speed of drawing rollers.

Taper package building on the bobbins is controlled by cam 16 and a ratchet wheel 21. Cam 16 is fixed on feed roller shaft 17 and has a slot for changing the lift of builder rail 18. Cam 16 moves lever 19 which is fulcrumed at 20. Lever 19 holds a ratchet wheel 21 and a holding catch 22 at its outer end. Cord 23 is coiled round the collar of ratchet wheel 21 and passes under a guide pulley 24 and over a guide pulley 25 and is connected to builder rail 18 preferably in the centre. When cam 16 rotates, it lifts lever 19, and ratchet wheel 21 is moved by one tooth by pushing catch 26 which in turn is supported on the framing. Holding catch 22 prevents the reverse motion of ratchet wheel 21. As ratchet wheel 21 rotates, cord 23 is shortened and a tapered package of yarn is formed on the bobbin.

In Fig. B, bearing plates 27 and 29 are provided with collars 30 and 31 respectively. The semi-circular bearing plate 28A overlaps the bearing plate 28. Both of them being semi-circular can swivel according to the position of the top rollers. Both the collars 30 and 31 are threaded. Bearing plates 28 and 28A have screws 32 and 33 secured to them respectively. The gauge between the bearing plates can be altered by rotating the collars 30 and 31 on screws 32 and 33 respectively. Springs 34 and 35 are secured to discs 36 and 37 and to screws 38 and 39 respectively. Screws 38 and 39 pass through threaded holes of plate 40. Spring 34 and 35 press bearing plates 27, 28, 28A and 29 and consequently the top rollers. Pressure can be altered by turning the screws 38 and 39. Plate 40 is secured to the framing of the top rollers.

In Fig. D, bearing plates 56, 57, 57A and 58 are provided with channels 59, 60, 61 and 62 respectively. Bearing plate 57A overlaps bearing plate 57 and both being semi-circular swivel according to the position of top rollers. Channels 59 and 62 have threaded holes in which screws 63 and 64 respectively are tightened. Channels 60 and 61 are slotted in the centre and overlap channels 59 and 62 respectively and slots coincide with screws 63 and 64 respectively. After adjusting the required gauge between the bearing plates 56, 57, 57A and 58, screws 63 and 64 are tightened to secure their positions.

In Fig. C, channel plates 41 and 44 are supported and slide on endless wires 45, and channel plates 42 and 43 are supported and slide on endless wire 46. Endless wires 45 and 46 are supported on pulleys 47 and 48 respectively. The latter are supported by screws 49 and 50 respectively which pass through framing 51. Screws 49 and 50 tighten endless wires 45 and 46 and prevent channel plates 41, 42, 43 and 44 from

Price : TWO RUPEES.

touching the drawing rollers 52, 53, and 54. Similar pulleys and screw arrangement is made at the framing 55, not shown in the drawings. Channel plates 41, 42, 43, and 44 increase cohesion of cotton fibres and prevent the falling off of the cotton fibres.

I claim :

1. Improved hand spinning wheel or charkha, the top drawing rollers of which are held in adjustable and swivelling bearing plates from the top with tension springs on them.

2. Improved hand spinning wheel or charkha as claimed in Claim 1 characterised in that the sliding channel plates are provided on wires between each pair of drawing rollers.

3. Improved hand spinning wheel or charkha as claimed in Claim No. 1 and 2 characterised in that a cam is fixed on the feed roller shaft imparting motion to the builder rail by means of a lever with a ratchet wheel secured at its outer end and the builder rail connected to the collar of the ratchet wheel by a cord supported by guide pulleys and the ratchet wheel being provided with a pushing catch and a holding catch.

4. Improved hand spinning wheel or charkha as claimed in Claims 1, 2 and 3 characterised in that the drawing rollers are directly driven by gear drive mechanism.

5. Improved hand spinning wheel or charkha as claimed in Claims 1 to 4 substantially as described and illustrated.

M. P. SHIKHARE.

Attorney for and on behalf of the Applicant.

Dated this 20th day of October 1961.

GIP Simla—GL—34 Patent/62—10-1-63—100.

No. 74644 of 1961.

No. of Sheets. 2.

Sheet No 1.

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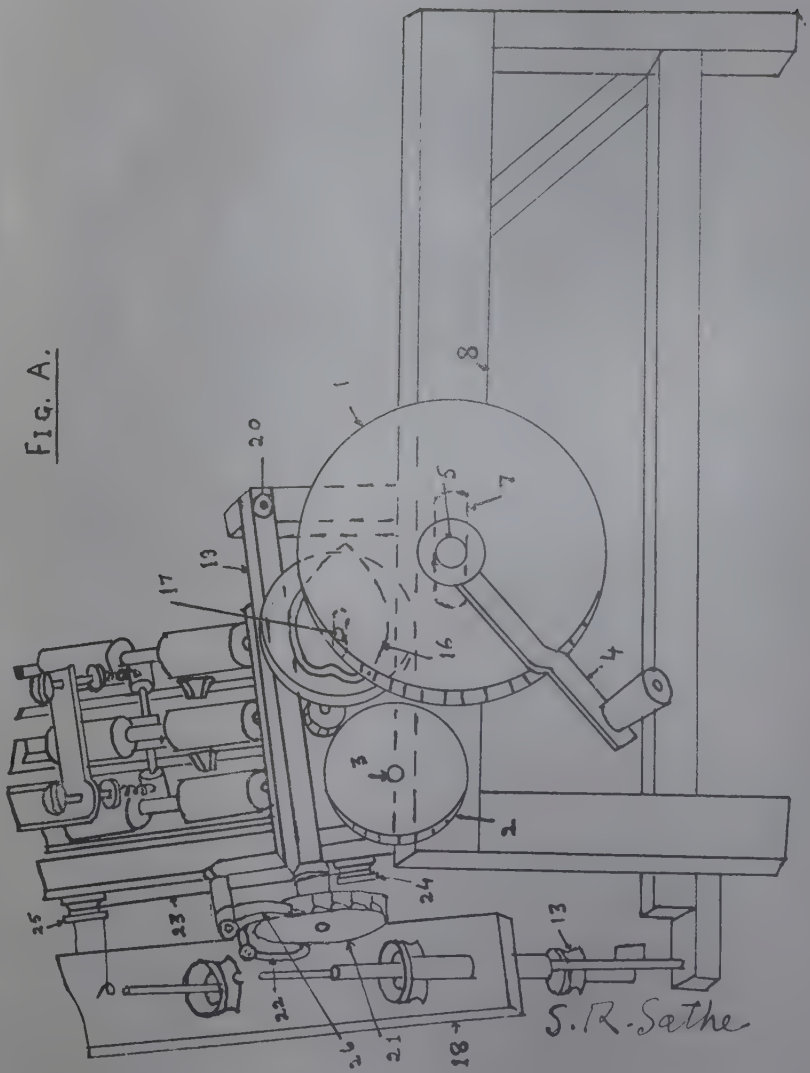
Ramchandra
Sathe.

FIG. A.



No. 74644 OF 1961.

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SATHE.

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FIG. B

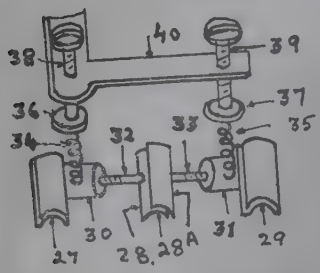
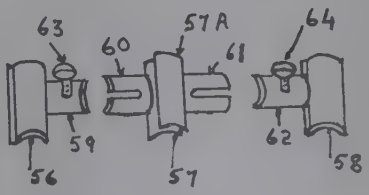


FIG. D.



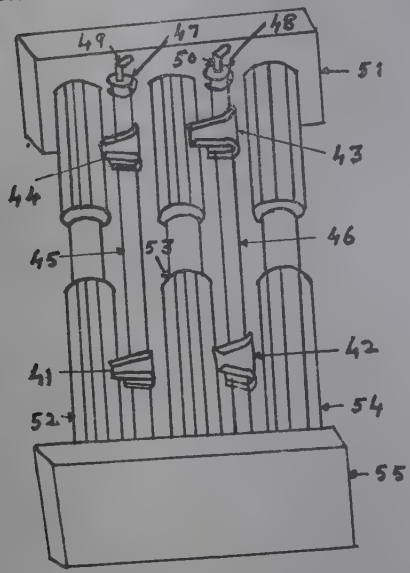


FIG. C.

S.R. Sathe.

...REPRODUCTION PROHIBITED

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74645, filed 23rd December 1960. (Accepted 5th April 1962.)

ELECTRIC LAMP FOR CYCLES.

MOHAMAD RAFI, Proprietor of the firm M. R. & Sons, Katra Raji, G. B. Road, Delhi, India. (Indian).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

There are various types of known electric lamps for cycles. All such lamps are provided with a switch mechanism comprising a press button actuated contacts adapted to be retained in their pressed down positions in which they keep the electric circuits closed, so that the lights are on; for putting off the lamps the said contacts are released.

The object of my invention is to provide an electric cycle lamp with a simple switch mechanism. Another object of my mechanism is to provide a simple construction of a cycle electric lamp. An electric lamp for cycles, according to my invention, is characterised in that its switch is in the form of a hook made of a metal which is in electric contact with the body or casing of the lamp and is adapted to be lowered to be brought into contact with a pole of an electric cell in the lamp for completing the electric circuit of the lamp and to be raised to break the said circuit, for switching the lamp on and off, respectively. The lamp according to my invention is illustrated in the accompanying drawings, in which :

Figure 1 shows a perspective of the lamp with parts of its casing, reflector and front glass shown partly broken off for showing the inner details;

Figure 2 is a rear view of the lamp with the cover of the casing open;

Figure 3 shows the front glass of the lamp;

Figure 4 shows a perspective view of the reflector;

Figure 5 shows the electric bulb;

Figure 6 shows a clamp for connecting the positive pole of the electric cell to the electric bulb;

Figure 7 shows the electric cell; and

Figure 8 shows a steel wire spring clip for holding the reflector and glass in position

The lamp shown in figures 1 and 2 has a casing consisting of a front portion 13 and a back cover 14; the cover is adapted to be retained in its closed position by means of a clip 15 hinged to the front part; this clip may be of any known construction. The front part 13 of the casing has a cylindrical socket extending to the front, within which the reflector 4 is housed. The reflector and the front glass are retained in position by means of a spring clip shown in figure 8; this clip is made preferably of steel wire bent into a generally circular configuration with rearwardly extending lugs one of which as shown in figure 8 is channel shaped and the other is U-shaped; the circular part of the clip bears against the glass whereas the said two lugs embrace the outer surface of the reflector and press onto the inner surface of the socket. The bulb 5 is screwed into the screwed socket at the rear of the reflector. A spring clamp or clip shown in figure 6 located in channels formed in a block of insulating resilient material such as a plastic, connects the positive pole of the electric cell 7 with the central terminal or pole of the bulb 5. The electric cell is retained in its inverted position shown in figure 1 by of the said clamp or clip 6 and an upper insulating block 10 of a resilient plastic material. A hook 9 made of a wire of conducting material for example copper or brass forms the switching device of the lamp. The hook 9 is shaped like an elongated loop having two inwardly directed ends disposed on opposite sides of the block 10. When the hook is lowered its inner ends will bear on the negative pole of the cell 7, constituted by the base of the container of the cell and be in electric contact therewith; the hook should then be turned at a right angle to the front; a pair of dents or projections 12, only one of which is shown in figure 1, will retain the hook in position without slipping off. The hook 9 being in electric contact with the metal surface of the casing which is electrically connected to the body of the bulb 5 through the reflector and the clamp (fig. 6) will complete the electric circuit, and light the lamp. By turning the hook 9 from the above described position to the left to a vertical position and lifting it, the electric circuit will be broken and the lamp put off.

My invention is not limited to the embodiment described and illustrated; modifications and alterations of the lamp described and illustrated within the scope of the following statement of claims are possible :

I claim :

1. An electric lamp for cycles is characterised in that its switch is in the form of a hook made of a metal which is in electric contact with the body or casing of the lamp and is adapted to be lowered to be brought into contact with a pole of an electric cell in the lamp for completing the electric circuit of the lamp and to be raised to break the said circuit, for switching the lamp on and off respectively.

2. An electric lamp as claimed in Claim 1 which has a body or casing having a front part and a back cover hinged to the front part and adapted to be retained by a spring clip in its closed position, the said front part having a forwardly extending socket within which a reflector with an electric bulb and a glass disc are located.

3. An electric lamp as claimed in Claim 2 in which the front glass disc and the reflector are held in position in the said socket by means of a spring clip.

4. An electric lamp as claimed in any of the preceding claims in which an electric cell is located in the casing or body thereof with one of its poles, for example the positive pole connected to a terminal of the bulb by means of a clip or clamp.

5. An electric lamp as claimed in any of the preceding claims in which the said hook is made of a wire of a metal for example copper or brass adapted to be lowered into electrical contact with negative pole of the cell and turned at right angles to the front and retained in this position to keep the lamp switched on.

6. A lamp as claimed in Claims 2-5 in which the clip for retaining the reflector and the front glass disc is made of steel wire and has a generally circular configuration with two lugs, one of a channel shape and other of U-shape adapted to bear on the reflector and the inside of the socket and retain the reflector and glass disc in position.

7. An electric lamp for cycles substantially as herein described and illustrated in the accompanying drawings.

R. P. ANAND,
N. K. ANAND,
OF THE ACME COMPANY,
Applicant's Agents.

Dated the 20th day of December 1960.

Price : TWO RUPEES.

MOIP Santh.—34 Patent/62—25-1-63—100.

ONE SHEET

No. 746 45 1960

APPLICANT: MOHAMAD RAFI

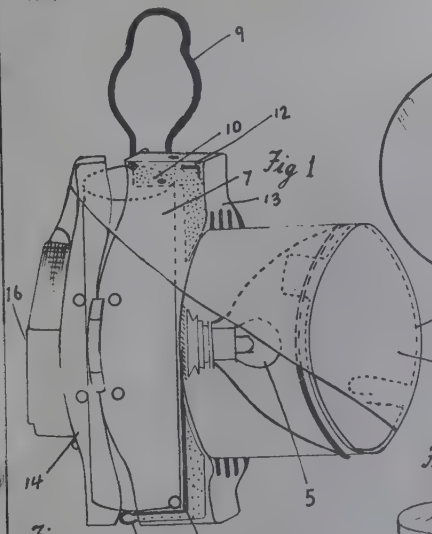


Fig 1

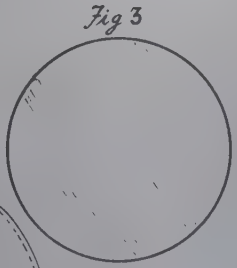


Fig 3

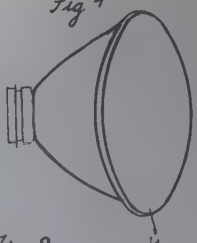


Fig 4

Fig 8

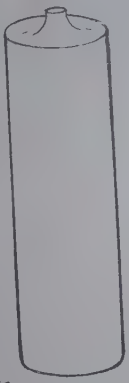


Fig 7

Fig 5

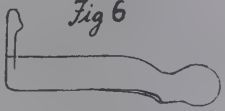


Fig 6

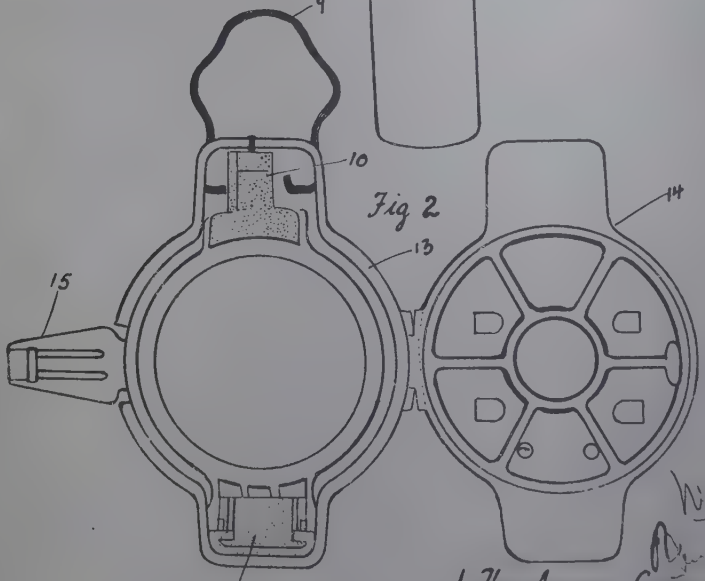


Fig 2

of The Acme Company

APPLICANTS AGENTS

REG. NO. 2273 E/44—108/52

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CENTRE

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.
Specification No. 74648, 23rd December 1960 2 Paus 1882 (Saka). (Accepted 5th May 1962.)

IMPROVEMENTS IN BAND BUILDING APPARATUS.

THE GOODYEAR TIRE & RUBBER COMPANY, MANUFACTURERS, A CORPORATION ORGANIZED UNDER THE LAWS OF THE STATE OF OHIO, UNITED STATES OF AMERICA, HAVING ITS PRINCIPAL PLACE OF BUSINESS AT 1144 EAST MARKET STREET, AKRON, COUNTY OF SUMMIT, AND STATE OF OHIO, U.S.A.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to an apparatus for building endless, flexible bands and, more particularly, is concerned with apparatus of this character for building rubberized cord fabric bands adapted to be incorporated into pneumatic tires.

It is the general object of this invention to provide an apparatus employing inextensible belts for building endless bands which is quickly adjustable to build bands of any desired but exact length, and with the apparatus functioning to accurately join together all portions of each band and with the apparatus constructed to permit quick removal of the completed band therefrom. Another object of this invention is to provide an apparatus for building bands in an exact circumferential length, free of folds, wrinkles, and with all the parts of the band being firmly joined together with air pockets.

The present invention, accordingly, provides an apparatus for building bands for pneumatic tires and the like comprising a pair of endless belts, means for effecting relative movement between the supports and the belts to position the belts in cooperative relationship with each other or in non-cooperative relationship with each other, one of said belts being inextensible and supported by at least four rotatable shafts, one of said shafts being driven by said one belt in a direction opposite to that of the other three shafts supporting said one belt whereby the circumferential length around said one belt may be varied.

The foregoing and other objects of this invention will be better understood by reference to the description and the accompanying drawings in which Fig. 1 is a front elevational view of the apparatus in operative position;

Fig. 2 is a fragmentary plan view of the apparatus with parts broken away and parts in cross section.

Fig. 3 is a fragmentary view similar to Fig. 1 showing the apparatus in inoperative position;

Fig. 4 is a schematic view similar to Fig. 3 showing the minimum and maximum adjustable positions of the apparatus.

In the drawings the numeral 10 indicates a frame from which the ends of a plurality of rollers 11, 12, 13, 14 and 15 are secured in cantilever relationship. The roller 11 is mounted on a shaft 16 rotatable in bearings 17 and 18 supported on the frame 10. The outer end of the shaft 16 is provided with a sprocket 19 driven by the motor 20 through a suitable drive belt 21. The rollers 12 and 13, respectively, are mounted on shafts 22 and 23, rotatable in pairs of bearings 24 and 25. The rollers 14 and 15 are respectively mounted on shafts 26 and 27 rotatable in pairs of bearings 28 and 29 supported on a carriage 30 a fixed distance apart. The carriage 30 is provided with a plurality of anti-friction rollers 31 which engage a pair of slides 32 and 33 on the frame 10 whereby carriage 30 is reciprocally movable relative to the slides 32 and 33.

The position of the carriage 30 is adjusted by means of a screw shaft 34 which threadedly engages a block 35 secured to the carriage and a block 36 secured to the frame 10. The end 37 of the screw shaft 34 is provided with suitable hand wheel 38. The end 39 thereof is fixed to a piston rod 40 secured to the piston 41 which is operable within the cylinder 42. The end 39 of the screw shaft 34 is rotatably connected to the rod 40 but is fixed thereto with respect to longitudinal movement. The rollers 11 through 15 cooperate to support an endless inextensible belt 43 which passes around all the rollers 11 through 15 in the same direction except roll 14. The belt 43 passes around the roller 14 in an opposite direction to that of the other rollers.

The belt 43 serves as the support on which the band built by the apparatus is constructed. In the drawings, the letter B has been used to indicate the band built on the apparatus. Preferably the band B is not supported with its entire periphery in engagement with the belt 43. A separate roller 44 mounted for rotation on the bracket 45, secured to the carriage 30, and a bracket 46 which is secured to the outboard ends of the rollers 44, 14 and 15. The band B is trained around the roller 44 and is thus separated from the belt 43 in the region of the roller 44.

From the foregoing it is seen that bands having various circumferential lengths can be readily built on the apparatus. As shown in Fig. 4 of the drawings the length of the band built on the apparatus is determined by the distance around the rolls 44, 15, 11, 12 and 13. Bands of maximum length are built on the apparatus with the rolls 14, 15, and 44 in the position shown in solid lines in Fig. 4, and bands of minimum length are built with the said rolls in the position shown in dotted lines in Fig. 4. As indicated above, the rolls 14 and 15 are moved between the two extreme positions shown in Fig. 4 by adjusting the position of the carriage 30 by means of the hand wheel 38. During such movement it is seen that the extensible belt 43 remains under constant tension and is entrained around the various rolls in a manner such that all of the rolls rotate in the same direction excepting the roll 14. As the carriage 30 is adjusted the length of belt between rolls 13 and 14 increases as the length of belt between rolls 11 and 15 decreases, and *vice versa* the increase being equal to the decrease because the said lengths or stretches of belt are parallel.

Associated with the belt 44 is a second endless belt 47 entrained around a pair of rollers 48 and 49. The roller 48 is maintained a fixed distance from the roller 49 by a member 50 which is supported at one end by a link 51 pivotably mounted at 52. An arm 53 is fixed to the link 51 and connected to an arm 54 by the adjustable link 55. The arm 54 is pivotably supported at 56 and is connected to the roller 49 at 57. The piston rod 58 of cylinder 59 is pivotably supported at 60 to a bracket 61 connected to the arm 51. Actuation of the cylinder 59 in the direction of the arrow shown in Fig. 1 rotates the arm 51 clockwise about the pivot 52 and simultaneously through the above described links and causes the arm 54 to likewise rotate about the pivot 56 whereby the rollers 48 and 49, which are respectively connected thereto move from the position shown in Fig. 1 to the position shown in Fig. 3 wherein the belt 47 is in non-cooperative position with the belt 43.

The outer end of roller 11 as shown in Fig. 1 is provided with a rotatable roll 62 which rests in a V-shaped notch 63 provided in the end 64 of arm 65 which is pivotably supported at 52. The arm 65 is connected to a link 66 by a link 67. As the cylinder 59 is actuated in the manner described above the link 66 rotates clockwise around the pivot 56 whereby the arm 65 is rotated counter-clockwise around the pivot 52 and is moved thereby to the position shown in Fig. 3.

After the band B has been built upon the belt 43 it is advantageous to firmly stich all the several plies of the band B together. A stitching roller 68 is rotatably supported at each end thereof on beams 69 pivoted at 70 to the frame 10. The ends 71 of the beams 69 are connected by a cross member 72 which is in turn connected to a cylinder 73 through piston rod 74. Actuation of the cylinder 73 causes the beams 69 to rotate counter-clockwise around the pivot 70 to thus raise the roller 68 under contact with the band B.

Those skilled in the art may readily provide suitable controls for effecting operation of the band building apparatus and its components in the desired sequence and by its relation, therefore no such control elements have been herein illustrated. Control levers, pedals, and the like, may be provided where necessary

to control the energization of the motor 20 and to energize solenoid valves, limit switches, or the like to admit or vent air under pressure from within the various actuating cylinders 42, 59 and 73. These controls are within the realm of erection by skilled mechanics and no invention is seen in using any of a variety of forms thereof which may be employed to accomplish the desired functions and the desired sequence as described herein.

Prior to building a band B the operator first adjusts the position of the carriage 30 and its associated rollers 14 and 15 so that the band built on the apparatus will be of the proper and exact circumferential length. The adjustment of the position of the rollers 14 and 15, which are supported a fixed distance apart is, of course, controlled by the rotation of the hand crank 33 which as described positions the carriage 30 at the desired location. The exact size of the band which can then be built on the apparatus will be indicated on the scale 75 by the pointer 76, the scale 75 being appropriately calibrated. Thereafter a ply, or length of band forming material, is fed to the apparatus from the right-hand side of the apparatus as viewed in Figs. 1 through 4. The ply of material is guided over the top of the belt 43 and the operator then energizes the motor 20 to drive the belt 43 in the direction shown by arrows in Fig. 1. The end of the ply material is carried around the belt 43 down between the belt 43 and belt 47 and is fed out by the belts at which point the operator catches the end of the ply material and folds it back over the roller 44. The operator then joins the two ends of the ply material to form the first ply of the band B. After the ply has been joined end to end the operator usually runs the first ply thus assembled several times around on the belt 43 so that he can see that the band is free from wrinkles and position the splice at a point remote from the splice of the next ply which will be built into the band. The cooperating action of the belts 43 and 47 is such that the first ply and any ply material built into the band is substantially free from wrinkles and the like. With the first ply of material positioned so that its splice is towards the far end of the belt 47 a second ply of material is built onto the first ply in substantially identical manner to that already described. In this fashion any additional number of plies can be built into the band in a relatively rapid and efficient manner.

Once the various plies have been built into the band, the cylinder 73 is actuated to lower the stitching roller 68 into engagement with the band. The motor 20 is also actuated to rotate the belt 43 and the band B beneath the stitching roller 68 to effect a positive and satisfactory stitching of the various plies. The cylinder 59 is then actuated in a direction shown by arrows in Fig. 1 to cause the rollers 49 and 48, the support 65, and the lower belt 47 to be moved into the inoperative position shown in Fig. 3. At the same time the cylinder 42 is actuated which moves the carriage 30 through the screw shaft 34 in a direction shown by the arrows in Fig. 2 which in turn moves the rollers 14, 15, and 44, in a direction shown in Fig. 3 of the drawings, a distance equal to the stroke of the piston 41 whereby the circumferential length around the belt 43 and roller 44 is substantially reduced, as shown in Fig. 3, so that the band B may be easily removed from the apparatus by merely slipping the belt axially of the roller supporting the belt 43 and endwise of the belt 43. After the band B has been removed from the aparatus the cylinder 42 is actuated to again position the carriage 30 and rollers 14 and 15 supported thereon into its adjusted position so that the construction of the next band can be initiated.

From the foregoing it will be recognized that the various objects of my invention have been achieved by the provision of improved apparatus for building endless bands of ply material which is relatively inexpensive and easily operated to rapidly and efficiently produce high quality bands of exact but in a desired length.

While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in the art that various changes and modifications may be made therein without departing from the spirit or scope of the invention.

We claim:

1. An apparatus for building bands for pneumatic tires and the like comprising a pair of endless belts, means for effecting relative movement between the supports and the belts to position the belts in cooperative relationship with each other or in non-cooperative relationship with each other, one of said belts being inextensible and supported by at least four rotatable shafts, one of said shafts being driven by said one belt in a direction opposite to that of the other three shafts supporting said one belt whereby the circumferential length around said one belt may be varied.

2. Apparatus as claimed in Claim 1 in which said oppositely driven shaft is supported a fixed distance from one of said other shafts, and means are provided for simultaneously moving said oppositely rotating shaft and said other shaft relative to said other shafts.

3. Apparatus according to Claim 1 including means for supporting the other belt so that unsupported stretches thereof are in opposed relationship to said one belt, means for moving the supporting means for said other belt to move it into engagement with said one of the belts, and means for rotating at least one of said shafts, at least two of said shafts being simultaneously movable relative to the other shafts whereby the circumferential length around said first belt may be varied.

4. An apparatus for building bands for pneumatic tires and the like including a pair of endless belts, means for moving at least one of the belts in an endless path, means for effecting relative movement between the supports for the endless belts to position the belts in cooperative relationship with each other or in non-cooperative relationship with each other, one of said belts comprising an inextensible endless belt, a plurality of rotatable shafts supporting said belt, said belt passing around one of said shafts in a direction opposite to its passage around said other shafts, and means for moving said one shaft and one of said other shafts relative to the remaining shafts.

5. Apparatus as claimed in Claim 4 in which one of said remaining shafts is positioned below a stitching roller, said one remaining shaft having a movable support at one end thereof and means for moving said support when said belts are moved in non-cooperative relationship.

6. Apparatus as claimed in Claim 4 in which said oppositely rotating shaft and said one other shaft are supported upon a carriage and means are provided for adjustably positioning said carriage member relative to said remaining shafts.

7. Apparatus as claimed in Claim 6 in which the portion of said belt extending from said oppositely rotating shaft is parallel to the portion of said belt extending from said one other shaft.

8. Apparatus as claimed in Claim 6 in which said positioning means comprises a screw shaft threaded to said carriage and means for rotating said shaft.

9. Apparatus as claimed in Claim 8 in which means are provided for moving said screw shaft, and in turn said carriage, a substantial distance in said plane, whereby the circumferential distance around said rolls is reduced to permit removal of the completed band.

10. Apparatus as claimed in Claim 9 in which said means for moving said screw shaft includes a fluid actuated cylinder having a piston connected to said shaft.

11. An apparatus for building bands for pneumatic tires and the like substantially as hereinbefore described with reference to and as shown in the accompanying drawings.

R. HALL,

OF REMFRY & SON.

Agent for the Applicants.

Dated this 23rd day of December 1960.

MOTT Smith – SL—39 Patent/62—7-3-63—100.

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74651, filed 23rd December 1960, 2 Paus 1882 (Saka). Reciprocity date (United Kingdom)—24th December 1959. (Accepted 23rd June 1962.)

METHOD FOR PRODUCING IMPROVED ARTIFICIAL POLYMERIC MATERIALS IN THE FORM OF FIBRES, FILAMENTS, FILMS, STRIPS, SHEETS AND THE LIKE SHAPED PRODUCTS.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, MANUFACTURERS, OF IMPERIAL CHEMICAL HOUSE, MILLBANK, LONDON, S.W.1, ENGLAND, A BRITISH COMPANY.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

The present invention relates to method for producing new and improved artificial polymeric materials in shaped forms such as filaments, fibres, films, strips, sheets and the like.

Shaped forms of linear solid crystalline polymers of aliphatic 1:2 mono-olefines, for example polyethylene, polypropylene and poly-4-methyl pentene-1, which include waterproofness, resistance to many commonly encountered organic liquids and chemical reagents, and varying degrees of tensile strength and extensibility, which at least in the case of polyethylene and polypropylene have enabled them find industrial uses. Thus polyethylene is widely employed in the manufacture of films and plastics and the highly crystalline high density variety has also found application in the manufacture of filaments for cordage. The crystalline varieties of polypropylene melting at temperatures above approximately 150°C are widely used in the production of plastics and are also in use for the manufacture of films, and are now being made into fibres and filaments intended for use in textiles. These crystalline polymers of aliphatic 1:2 mono-olefines, however, suffer from the disadvantage that they cannot readily be dyed by any of the processes normally used in the dyeing of textiles and films, and they have a pronounced tendency to become electrostatically charged in normal usage, which for some purposes is an inconvenience.

Thus although the physical properties of crystalline polyethylene and polypropylene render them outstanding for certain industrial applications, for example ropemaking, their applicability, especially in the textile field, has hitherto been limited by their unreceptivity for the commonly used dyestuffs, and also by their excessive tendency to acquire electrostatic charges.

The new and improved artificial polymeric materials of the present invention are derived from the aforesaid polymers, and in the form of filaments, fibres, films, strips, sheets and the like shaped articles retain to a significant degree the desirable tensile properties of the above mentioned crystalline polymers of aliphatic 1:2 mono-olefines, but they have a more appreciable degree of absorbency for moisture, and in marked contrast to the articles made of the last mentioned materials they do not acquire static electric charges under normal conditions of usage, and they readily accept a wide variety of acid wool dyes. This combination of properties renders the filaments and fibres of particular value as textile materials and also renders the films, sheets, strips and the like of considerable interest.

The new and improved polymeric materials of the present invention are in fact made by a process in which a solid crystalline polymer of an aliphatic 1:2 mono-olefine is used as the starting material, but the chemical nature of the final materials is very different indeed from that of the starting materials.

According to the present invention the new and improved artificial polymeric materials in shaped forms comprise throughout their thickness an intimate association wholly in the polymeric state of an aliphatic 1:2 mono-olefine and styrene such that the aliphatic constituent of said polymeric association is crystalline, wherein for at least an appreciable distance inward from the surface of the shaped form the aromatic constituent of said polymeric association is modified by the possession of substituent groups in the benzene nucleus which contain quaternary ammonium salt groups, the proportion of the aromatic constituent reckoned as styrene to the aliphatic 1:2 olefine constituent being from 2·5 to 10.

The aromatic constituent throughout the whole thickness of the intimate polymeric association constituting the material of the shaped form may, if desired, be modified by the possession of the substituent groups which contain quaternary ammonium salt groups, in which case the shaped form will be capable of being dyed throughout its whole thickness with appropriate dyestuffs, but for practical purposes it will not always be necessary that the dyestuffs should penetrate throughout the whole thickness of the shaped form, it being necessary only that abrasion resulting from the usage in handling or in service should not reveal patches of undyed material. As will be understood, it is the presence of the quaternary ammonium salt groups that confers the dyeing properties, and since in putting the invention into effect it is possible to control the depth to which the modification of the aromatic constituent by the substituent groups containing the quaternary ammonium salt groups takes place, and no difficulty is experienced in getting the dyestuff to penetrate into the interior of the shaped form having its aromatic constituent so modified, the depth to which it can be dyed is easily controlled. By the term "at least an appreciable distance inward from the surface" we mean anything more than the molecular layer actually exposed at the surface.

Thus the invention consists in the method of producing new or improved artificial polymeric materials in shaped form which comprises the steps of exposing a crystalline linear polymer of an aliphatic 1:2 mono-olefine in comminuted form to contact with from 2½ to 10 per cent by weight of liquid styrene monomer reckoned on the total hydrocarbon material, so that the liquid styrene monomer becomes uniformly distributed in and wholly imbibed in said crystalline linear polymer, subjecting the imbibed styrene *in situ* to a polymerisation treatment at a temperature insufficient to render the particles of the resulting thermoplastic polymeric association coalescent, shaping the resulting still discrete particles into the desired shaped form, and thereafter treating it with a halogeno-alkylating agent and subsequently with a tertiary amine so as to effect nuclear substitution of the aromatic constituent of the polymeric association constituting the material of the shaped form with groups containing quaternary ammonium salt groups to an appreciable distance inward from the surface.

The dyestuffs to which the resulting shaped forms are specifically receptive and with which they can be dyed to the greatest distance from their exposed surface are Acid Wool dyestuffs, *e.g.*, Azo Geranine 2 G 200, Naphthalene Orange G 125, Lissamine Fast Yellow 2 G 125, Lissamine Green V 200, Solway Blue PFN 125, Solway Green JS or Naphthalene Red JS.

The extent to which the dye receptive quaternary ammonium groups and hence to which the dyeing effect will extend inwards from the surface depends both on the time and conditions of the chemical treatments with the halogeno-alkylating agent and the tertiary amine and on the percentage of the aromatic constituent in the polymeric association. In general the higher the percentage of the aromatic constituent within the set limits, the higher is the rate at which the dyestuff will penetrate. In general the quaternary ammonium salt formation from the halogeno-alkylated aromatic constituent occurs more rapidly than does the halogeno-alkylation of the aromatic constituent, so that it is sufficient to allow the same time for quaternisation that has been allowed for halogeno-alkylation.

In putting the invention into effect, the linear crystalline polymer of the aliphatic 1:2 mono-olefine used, which may be, for example, low density polyethylene, high density polyethylene or isotactic polypropylene, may be in the form of cut-up film or chopped filaments, threads or yarns, but is preferably in the form of granules or a granular powder. Monomeric liquid styrene is mixed into

this material in presence of a polymerisation catalyst, which is preferably a catalyst of the free radical type, for example, benzoyl peroxide, azo-di-isobutyronitrile, tertiary butyl peroxide, cumenehydroperoxide or di-cumyl peroxide, until the styrene has been well distributed throughout the particles and completely imbibed. The catalyst is preferably first dissolved in the styrene, whereupon the liquid and solid ingredients may be tumbled together. This operation may be conducted at atmospheric temperature, but preferably at a raised temperature insufficient to effect any polymerisation, for example, 50 to 70°C. Since the presence of atmospheric oxygen in some cases seriously hinders the subsequent polymerisation, which is affected at a higher temperature, which, however, must be insufficient to cause the still discrete particles to coalesce, it may be necessary to carry out the imbibition and polymerication steps in an atmosphere of an indifferent gas such as nitrogen. In the case of polyethylene the polymerisation temperature should not exceed about 100°C in order to prevent any coalescence of the particles. In the case of polypropylene the temperature may be a little higher, but since monomeric styrene boils at about 146°C it is desirably below 110°C unless the operation is conducted under pressure, in which case a temperature up to about 130°C may be employed.

The polymerised product should be of homogeneous appearance and infra-red analysis should indicate that the aromatic constituent is uniformly distributed in each individual particle.

The product is thermoplastic and when sufficiently heated it fuses. With the assistances of heat the mass of discrete granules is now shaped into the desired final form and in that form is subjected to the treatment that introduces the dye receptive ionic groups, which is a 2 stage treatment of which the first stage is a treatment with a halogeno-alkylating agent which is preferably a chloromethylating agent, the second stage being a treatment with a tertiary amine. The first stage is preferably carried out in the presence of a Friedel Crafts reaction catalyst, for example, stannic chloride, zinc chloride, aluminium chloride, titanium tetrachloride or boron trifluoride. The halogeno-alkylating agent may be for example, methylchloromethyl ether, bis-chloroethyl ether, or chloromethylethyl ether. The treatment is preferably carried out at the boiling point of the reagent under reflux and may conveniently be done by passing the shaped article through a bath containing a large amount of the halogeno-alkylating agent. The excess of halogeno-alkylating agent and traces of catalyst adhering to the shaped product are removed, for instance by washing with water or a combination of evaporation and washing, or by treating the material with a water soluble organic solvent for the said reagent and then with water.

The resulting shaped product in which the aromatic constituent of the polymeric association has been halogeno-alkylated nuclearly is then treated with tertiary amine, preferably trimethylamine, dimethylethanolamine or diethylethanolamine. Triethanolamine or methyltriethanolamine may also be used but since they react less readily, it may be advantageous to increase the temperature of treatment. The resulting product is washed to remove excess of the tertiary amine, for example, by washing successively with water dilute acid, and water again.

As has been stated, the halogeno-alkylation reaction usually proceeds more slowly than the quaternisation reaction, and accordingly it is usually sufficient for the duration of the treatment with the tertiary amine to be equal to that of the treatment with the halogeno-alkylating agent. The rate of progress of the modification of the aromatic constituent in the shaped form can usually best be assessed by microscopic observation of the depth of penetration by an acid wool dyestuff from an acid dyebath of predetermined composition applied always in the same way after periods of treatment of progressively increasing duration with the aforesaid modifying reagents. Examination of the transverse section of a filament or film under microscope will reveal whether the dyestuff has penetrated completely through it or whether there is an undyed inner portion, in which latter case it is possible to assess the rate of progress of the modification of the aromatic constituent of the polymeric association by examination of the thickness of the dyed zone or zones as the case may be as compared with the thickness of the whole filament or film, and in this way the duration of the treatment with the halogeno-alkylating agent may be controlled so that a predetermined depth of modified zone will be obtained, provided that the halogeno-alkylation reaction is slower than the quaternisation reaction for the particular compounds used and that the exposure to the tertiary amine is sufficient to enable the chloroalkylated zone to be fully quaternized. The invention is further illustrated in the following Examples in which all parts and percentages are by weight.

Example 1

450 gm. of a granular isotactic polypropylene of molecular weight 200,000 was introduced along with twice its weight of 12 mm. diameter steatite balls into a 2 litre bottle having closure means connectable at will to a source of vacuum, a nitrogen cylinder, or a liquid feed. The particle size distribution of the polypropylene was as follows:

retained on 60 mesh B. S. Screen	...	... (aperture 0.252 mm.) 2%
passing 60 and retained on 72 ,, ,, ,,	...	... (aperture 0.214 mm.) 7%
passing 72 and retained on 150 ,, ,, ,,	...	... (aperture 0.104 mm) 78%
passing150 and retained on 200 ,, ,, ,,	...	... (aperture 0.76 mm.) 10%
passing 200 ,, ,, ,,	...	... 3%

The air was exhausted and replaced by oxygen free nitrogen, the evacuation and refilling being repeated three times. 34 gm. freshly distilled styrene containing 1% of its weight of benzoyl peroxide dissolved in it was then added to the bottle, which was then rotated on rollers in an oven whose temperature was gradually raised over 4 hours to 100°C by which time the styrene had become completely absorbed in the granules. The bottle was then left stationary for 16 hours in the oven, whose temperature was held at 100°C. By this time polymerisation was practically complete, as evidenced by the fact that the granular product gave only about 0·2 to 0·4 per cent of volatile matter when heated at 65°C. for 1¼ hours at 0·2 mm. pressure. It weighed very nearly 484 gm.

The resulting granules were converted into sheets by compression between two steel plates at 90°C. under a pressure of 120 atmospheres, the sheets formed after the first compression being folded and recompressed several times. In this way the product was converted into films of ·0·233 mm. thickness. The sheets were opaque and white, but of regular appearance, and were hard but flexible.

The sheets were cut into strips and immersed for 120 minutes in a large bulk of boiling chloromethyl methyl ether containing 1% of its weight of zinc chloride as chloromethylation catalyst, under reflux. The strips were then washed with industrial methylated spirits and were immersed for 2 hours in a large bulk of aqueous solution of trimethylamine of 30-33% concentration. Finally the strips were washed successively in water, 5% hydrochloric acid solution and water again, until neutral. The resulting strips were of the same appearance as before the treatment with chlorimethyl methyl ether and trimethylamine and somewhat more opaque than polypropylene sheets. When treated in an acid dyebath containing 10% sodium sulphate decahydrate, 5% sulphuric acid and 0·2% Azo Geranine 2G 200 they were found to be dyed through and through.

Example 2

The procedure was the same as in Example 1 except that only 24 gm. of the styrene containing 1% of its weight of benzoyl peroxide were used instead of 34 gm. After the polymerisation treatment the product weighs

very nearly 474 gm. and the loss in weight after 1¼ hours heating at 65°C. at 0·2 mm. was 0·25-0·3%. After the treatments with chloromethyl methyl ether and trimethylamine the strips were found to be dyed in the Azo Geranine 2G 200 dyebath to a depth of 0·98 mm. inwards from each surface. After drying for 1 hour at 80°C and exposure to the atmosphere for 10 minutes they were tested for electrostatic properties by rubbing them under controlled conditions over an area of 2·54 cm. × 2·54 cm. and the electrostatic charge was determined by the Faraday Ice pail method. No charge was detectable, whereas a test of the strip before the treatments with chloromethyl methyl ether and trimethylamine gave a charge of $1{\cdot}60 \times 10^{-10}$ coulombs per sq. cm.

Example 3

The preparation of the granular product containing the styrene constituent in polymeric form was the same as in Example 2. Instead of being converted into sheet, however, it was spun in known manner into three-filament yarns of 40 denier, undrawn, and thereafter subjected to treatment successively with chloromethyl methyl ether and trimethylamine in the manner described in Example 1, but for a period of only 60 minutes with each reagent. It was found that the filaments of the yarn were dyed through and through when subjected to the dyebath referred to in Example 1. The water absorption at 20°C. was 2·04% and the water retained at 20°C in an atmosphere of 75% relative humidity was 1·67%. The yarns floated on water but the handle of the yarns was warm to the touch and generally pleasant for textile applications. The corresponding water absorption and retention of isotactic propylene fibre of the same molecular weight were less than 0·01%. The yarn showed no tendency to acquire electrostatic charges.

Example 4

The preparation of the granular polymeric product containing the styrene constituent in polymeric form was the same as in Example 2. Instead of being converted into sheet, however, it was spun in known manner into three-filament yarns of 11 denier drawn filaments, and thereafter subjected to treatment successively with chloromethyl methyl ether and trimethylamine in the manner described in Example 1, but for peroids ranging from 30 to 120 minutes, which were always the same for the two different reagents. The water absorption at 20°C and moisture retention at 20°C in an atmosphere of relative humidity and the dyeing properties were as follows:—

Chloromethyltion and amination each for 30 minutes :	Water absorption 1.00% Moisture retention 0.84%
" " " " " 60 "	Water absorption 1.39% Moisture retention 1.22%
" " " " " 60 " followed by dyeing with Napthalene Orange	Water absorption 1.20% Moisture retention 1.00%
Chloromethylation and amination { each for 30 minutes	Depth of penetration in Azo Geranine 2 G 200 dyebath as used in Example 1. 0.003 mm. (first sample)
" " 60 minutes	0.008 mm. " "
" " 120 minutes	Complete
" " 120 minutes	0.010 mm. (second sample)
" " 180 minutes	Complete (second sample)

Filamentary products in accordance with the invention dyed with Acid Wool dyes are unaffected in colour by normal laundering treatments with soap or synthetic detergents, or by immersing them in dry cleaning liquids such as chlorinated aliphatic hydrocarbons or light petroleum. This applies even when there is only a thin dyed zone surrounding an undyed core in each filament. Films dyed with Acid Wool dyes are correspondingly fast dyed. The tensile strength and extensibility of the filamentary products are such that they can be made into satisfactory textiles.

We claim:

1. A method of producing new or improved artificial polymeric materials in shaped form wherein a crystalline linear polymer of an aliphatic 1:2 mono-olefine in comminuted form is subjected to contact with from 2½ to 10 per cent by weight of liquid styrene monomer reckoned on the total hydrocarbon material, so that the liquid styrene monomer becomes uniformly distributed in and wholly imbibed in said crystalline linear polymer, subjecting the imbibed styrene *in situ* to a polymerisation treatment at a temperature insufficient to render the particles of the resulting thermoplastic polymeric association coalescent, shaping the resulting discrete particles into the desired shaped form, and thereafter treating it with a halogenoalkylating agent, and subsequently with tertiary amine so as to effect nuclear substitution of the aromatic constituent of the polymeric association constituting the material of the shaped form with groups containing quaternary ammonium salt groups to an appreciable distance inward from the surface.

2. A method as claimed in Claim 1 wherein the linear crystalline polymer of the aliphatic 1:2 olefine used is isotactic polypropylene.

3. A method as claimed in Claim 1 wherein the linear crystalline polymer of the aliphatic 1:2 olefine used is polyethylene.

4. A method as claimed in any one of Claims 1 to 3 wherein the monomeric liquid styrene is mixed into the linear crystalline polymer of the aliphatic 1:2 olefine in the presence of a free radical type polymerisation catalyst.

5. A method as claimed in any one of Claims 1 to 4 wherein the treatment of the crystalline polymer of the 1·2 aliphatic olefine with the styrene is conducted at a raised temperature preferably 50 to 100°C, insufficient to effect any polymerisation.

6. A method as claimed in any one of Claims 1 to 5 wherein the treatment of the crystalline polymer of the 1:2 aliphatic olefine with the styrene and the polymerisation treatment *in situ* is carried out in an atmosphere of an indifferent gas.

7. A method as claimed in any one of Claims 1 to 6 in which the shaping of the discrete granules into the desired final shaped form is carried out with the assistance of heat.

8. A method as claimed in any one of the preceding claims wherein the treatment with the halogeno-alkylating agent is carried out in the presence of a Friedel Crafts reaction catalyst.

9. A method as claimed in Claim 8 wherein the treatment with the halogeno-alkylating agent is carried out by passing the shaped form through a bath containing a large amount of said agent at its boiling point under reflux.

10. A method as claimed in any one of the preceding claims wherein the halogeno-alkylating agent is methyl chloromethyl ether.

11. A method as claimed in any one of the preceding claims wherein the tertiary amine is applied in amount and for a time sufficient to ensure complete conversion of the halogeno alkyl groups introduced into the shaped form to be completely quaternised.

12. A method as claimed in Claim 11 wherein the tertiary amine is trimethylamine.

13. A method for the production of new or improved polymeric film as claimed in any one of the preceding Claims 1, 2 and 4 to 12.

14. A method for the production of new or improved polymeric materials in filamentary form as claimed in any one of the preceding Claims 1, 2 and 4 to 12.

15. New or improved polymeric artificial materials in film form when produced by the method claimed in Claim 13.

16. New or improved polymeric artificial materials in filamentary form when produced by the method claimed in Claim 14.

17. New or improved artificial materials in shaped form whenever produced by the process claimed in any of Claims 1 to 14, dyed with Acid Wool dyes.

R. HALL

or REMFRY & SON,

Agent for the Applicants.

Dated this 23rd day of December 1960.

MGIP Sauth.—SL—106 Patent/62—19-9-63—100.

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74652, 23rd December 1960, 2 Paus 1882 (Saka). (Accepted 22nd June 1962.)

FLAME RETARDANT CELLULAR FOAMED ALKENYL AROMATIC RESIN PRODUCTS.

THE DOW CHEMICAL COMPANY, A CORPORATION OF THE STATE OF DELAWARE, UNITED STATES OF AMERICA, HAVING A PLACE OF BUSINESS AT MIDLAND, MICHIGAN, UNITED STATES OF AMERICA, MANUFACTURERS.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to flame retardant cellular foamed alkenyl aromatic resin products.

It is known to prepare flame-resistant, non-flammable or self-extinguishing cellular bodies of thermoplastic alkenyl aromatic resins by incorporating with the gel of a volatile organic compound and a normally solid flammable thermoplastic alkenyl aromatic resin such as polystyrene, certain organic bromides that are compatible with the resins in proportions sufficient to render the resins non-flammable, or self-extinguishing and thereafter extruding the gel into a zero of lower pressure.

In the heretofore known methods for making cellular bodies from thermoplastic alkenyl aromatic resins it is common practice to incorporate with the gel a small proportion of a finely divided filler such as calcium silicate or diatomaceous earth as an aid in controlling the size of the cells in the foamed product and to produce cells of smaller size.

However, the incorporating of silica or silicon-containing compounds in small amounts into the gel or on surfaces of the resin body has certain disadvantages. More particularly, it has been observed that the silica even when present in trace amounts has a pronounced action of increasing the flammability of an already flammable polymer, *e.g.*, polystyrene. Thus, the heretofore commonly employed practice of incorporating of silica-containing compounds such as calcium silicate, diatomaceous earth or silicone oils with flammable thermoplastic organic polymers such as the alkenyl aromatic resins, as an aid in controlling the pore size of the cells when the polymers are foamed to produce cellular articles, has not only the desired effect of decreasing the size of the cells, but has the undesirable action of increasing the flammability of the foamed product. These disadvantages are not found in the novel cellular foamed articles of the present invention.

The novel articles are obtained from alkenyl aromatic resins such as polystyrene or its copolymers, and are made flame-retardant or self-extinguishing by a content of a flame-proofing agent with the improvement that they contain, in addition, an indigo compound which not only acts as a nucleating agent, but has a decided effect on improving the flame-retardance and self-extinguishing properties of the polymeric articles, when it is employed in combination with a flame-proofing agent.

The present invention accordingly provides a cellular foamed alkenyl aromatic resin product which is made flame-retardant or self-extinguishing by a content of a flame-proofing agent, characterized in that it contains as a synergist an indigo compound. Quite often, it is possible to employ the flame-proofing agent in a proportion which is smaller than would be required to achieve the same flame-proofing effect in the absence of the indigo compound. Satisfactory enhancement of the flame-retardance is generally obtained if the indigo compound is present in a proportion ranging from 0·001 to 3 per cent. by weight based on the weight of the polymer. The preferred flame-proofing agents are organic bromine containing compounds which contain a plurality of bromine atoms attached to carbon atoms in an aliphatic or cycloaliphatic ring and which contain, preferably, at least 45 per cent. by weight of the organic bromine.

The indigo compounds as employed in accordance with the present invention do not only offer the above-stated improvements in the burning qualities of the products, but do also tend to control the size of the individual cells, making it possible to produce articles having primarily individual, closed thin-walled cells of exceptionally small size and uniformity. It is quite unexpected that the foamed articles of the present invention have this combination of properties and advantages.

The novel foamed articles of the present invention may be readily prepared by incorporating with an alkenyl aromatic resin such as polystyrene, or a copolymer of methyl methacrylate and styrene, or a mobile or flowable gel thereof, comprising the organic polymer having dissolved therein under pressure a volatile organic compound such as methyl chloride, pentane, or petroleum ether, a flame-proofing agent and an effective proportion of a finely divided organic indigo compound such as indigotin, bromindigotin, thioindigotin and the like, including the nuclear halogen and alkyl substituted derivatives of indigotin and thioindigotin, and thereafter foaming the polymer or the gel in known ways to produce a cellular article composed for the most part of uniformly fine individually-closed thin-walled cells.

The synthetic organic polymers to be employed in the invention can be any normally solid homopolymer or copolymer of one or more monovinyl aromatic compounds or copolymers containing in chemically combined, *i.e.*, polymerized or copolymerized, from at least 50 per cent. by weight of at least one polymerizable alkenyl aromatic compound having the general formula:

$$Ar—\overset{R}{\overset{|}{C}}=CH_2$$

wherein Ar represents an aromatic hydrocarbon radical or a nuclear substituted aromatic halohydrocarbon of the benzene series, and R is hydrogen or the methyl radical. The homopolymers and copolymers of one or more monoalkenyl aromatic compounds and copolymers containing in chemically combined form at least 50 per cent. by weight of at least one alkenyl aromatic compound having the above general formula are commonly known as "alkenyl aromatic resins". Examples of such alkenyl aromatic resins are the solid homopolymers of styrene, vinyltoluene, vinylxylene, Ar-ethyl-vinylbenzene, isopropylstyrene, tert.-butylstyrene, Ar-chlorostyrene, Ar-dichlorostyrene, or Ar-bromostyrene ; the solid copolymers of two or more of such alkenyl aromatic compounds with one another ; and solid copolymers of one or more of such alkenyl aromatic compounds wtih other readily polymerizable monoolefinic compounds such as methyl methacrylate or acrylonitrile. Copolymers of methyl methacrylate and one or more alkenyl aromatic compounds such as styrene, vinyltoluene or Ar-dichlorostyrene, in any proportions, *e.g.*, from 1 to 99 per cent. by weight of the methylmethacrylate and correspondingly from 99 to 1 per cent. of the alkenyl aromatic compound(s), can also be used, especially copolymers of from about 60 to 65 per cent. of methyl methacrylate and from 40 to 35 per cent. of styrene.

The indigo compounds to be employed in the invention can be indigotin, its derivatives such as bromo-indigotin, dibromo-indigotin, tetrabromo-indigotin, indigotin white, indigotin disulfonic acid, alkali metal salts, or sulfur analogues of the indigotin group wherein the NH groups of the indigotin have been replaced by S, and derivatives thereof, *e.g.*, thio-indigotin or 6,6′-dichloro-4,4′-dimethyl thio-indigotin. Such materials are represented by the general formula of the accompanying drawings, wherein R represents a radical of the group consisting of -NH- and -S- radicals, X and Y each represents a member of the group consisting of hydrogen, halogen and lower alkyl radicals containing from 1 to 4 carbon atoms, and Z is a member of the group consisting of hydrogen, halogen and the sulfonate radical of the formula $-SO_3M$, wherein M is an alkali metal. The indigotin, thio-indigotin or

derivatives thereof employed as the nucleating agents can be used in proportions of from 0·001 to 3, preferably from 0·02 to 0·5, per cent by weight of the thermoplastic organic polymer.

Examples of suitable indigotin (indigo), its derivatives or analogues such as the thio-indigotin or derivatives thereof which can be used in the invention are indigotin white, indigotin, 5-bromo-indigotin, 5,5′ - dibromo - indigotin, 5,5′,7,7′-tetrabromo-indigotin, 5,5′-indigotin disulfonic acid disodium salt, 5,5′-dibromo-7,7′-diethyl indigotin, 7,7′-dibromo-5,5′-diisopropyl indigotin, 5,5′-diethyl indigotin, 7,7′-diethyl indigotin, 5,5′-diisopropyl indigotin, 7,7′-dibromo-5,5′-diisopropyl indigotin, 6,6′-dimethyl indigotin, 7,7′-dimethyl indigotin, X,5,5′-7,7′-pentabromo indigotin, 3,3′-disulfonic acid, 5,5′,7,7′-tetrabromo indigotin disodium salt and 6,6′-dichloro-4,4′-dimethyl thio-indigotin, or mixtures of any two or more of such compounds.

Volatile organic compounds to be employed as the foaming agent for expending the heat-softened synthetic organic polymer or a mobile gel thereof can be petroleum ether, pentane, hexane, heptane, methyl chloride, dimethyl ether, methyl ethyl ether, monochlorodifluoromethane, butylene, isobutylene, butane pentane, iso butane, heptane, hexane or petroleum ether or certain perchlorofluorocarbons known *per se*. Mixtures of any two or more of such volatile organic compounds can also be used. The volatile organic compounds are generally employed in amounts of from 0·05 to 0·4 gram molecular proportion of the volatile organic compound(s) per 100 grams of the organic polymer initially used. Most advantageously, the improved foamed articles of the invention may be produced by a process which comprises feeding a solid granular organic polymer, *e.g.*, granular polystyrene, to a first section of a plastics extruder where in it is pressed by flights of a forwarding screw and is heated to its melting temperature or thereabout. The molten polymer is forwarded around or through a sealing plate or disc on a mid-section of the screw, thereby forming a plastic seal against counter-current flow of gas through the barrel of the extruder, and into a second mixing section of the extruder wherein it is mixed with a volatile organic compound, *e.g.*, methyl chloride, dimethyl ether, pentane, dichlorodifluoromethane and the like, which is fed under pressure to the mixing section of the extruder. The resulting mixture is agitated, cooled and forwarded into a mixer cooler wherein the ingredients are thoroughly blended and is brought to a uniform temperature between 60° and 130°C., preferably from 90° to 120°C., under pressure, then is extruded through an orifice into a zone of sufficiently lower pressure, *e.g.*, the atmosphere, to cause expansion of the extruded material with resultant formation of a cellular article.

The indigo compounds of the invention can be incorporated with the organic polymer by feeding said agents together with the granular polymer to the feed hopper of the plastics extruder or by feeding the nucleating agents into the stream of the heat-softened polymeric material, suitably just prior to or after its entry into the mixer cooler or at the same time as feed of the volatile organic foaming agent is admixed with the molten polymer. The subsequent blending of the mixture of the materials with one another serves to uniformly distribute the nucleating agents throughout the body of the flowable gel under pressure prior to its extrusion into a zone of lower pressure. The nucleating agents may constitute trace amounts, *e.g.*, 0·5 per cent. by weight or less, of a surface active agent such as sodium alkyl sulfonate, alkyl phenyl polyethylene glycol ether, sodium lauryl sulfate and the like, but such additives are not required in the invention.

Among the flame-proofing agents are to be mentioned as the most suitable the organic bromides which are derived from an aliphatic or cycloaliphatic hydrocarbon and which contain a plurality of bromine atoms constituting preferably at least 45 per cent. by weight of the molecule. Others are certain haloalkyl aromatic hydrocarbons and polybromoalkyl esters or ethers known *per se* to improve the burning proportions of the polymer.

Examples of suitable organic bromides are alpha,-beta-dibromoethylbenzene, 1,2-di (dibromomethyl)benzene di-(2,3-dibromopropyl) ether, 2,3-dibromopropyl propionate, tris-2(2,3-dibromopropyl)phosphate, carbon tetrabromide, tetrabromoethylene, 1,2-dibromo-1,1,2,2-tetrachloroethane, 1,1,2,2 - tetrabromoethane, dibromochloromethane, 1,2 dibromo-1,1-dichloroethane, 1,2-dibromo - 1,2,2 - trichloroethane, 1,2,3,4-tetrabromobutane, 1,2,3-tribromopropane, 1,2,4 - tribromobutane, tetrabromopentane, pentabromoethane, hexabromoethane, hexabromocyclohexane pentabromomonochlorocyclohexane, tetrabromodichlorocyclohexane and tribromotrichlorocyclohexane.

The flame-proofing agents and particularly the organic bromide are advantageously employed in amounts of from about 0·5 to 10 per cent. by weight of the alkenyl aromatic resin used. The organic bromide can be incorporated with the resin in a manner similar to that described with respect to the mixing of the indigotin or indigotin derivative nucleating agent, i.e., the organic bromide can be fed to the plastics extruder together with the granular polymer or it can be mixed with the stream of the heat-plastified materials at any point in the process prior to its extrusion into a zone of lower pressure. Best results are usually obtained by mixing the organic bromide with the stream of the materials in the mixer cooler, *i.e.*, after the molten polymer and the volatile organic compound have been mixed together under pressure and have been cooled to a temperature of about 150°C. or below. After mixing of the whole of the ingredients with one another under pressure in the process, the ingredients are subsequently blended into a homogeneous flowable gel which is brought while under pressure to a suitable temperature throughout its mass just prior to the point of discharge from the mixer-cooler and is then extruded into the atmosphere to produce a cellular article containing the nucleating agent and the organic bromide self-extinguishing agent uniformly distributed throughout. When making self-extinguishing foams wherein an organic bromide is incorporated with the organic polymer or a flowable gel thereof, it is advantageous to also incorporate a small amount, *e.g.*, from about 0·01 to 0·5 per cent. by weight, based on the weight of the polymer, of an acid acceptor such as sodium acetate, magnesium oxide, magnesium hydroxide, zinc oxide, calcium oxide, calcium carbonate, sodium bicarbonate and the like to neutralize trace amounts of hydrobromic acid which may be formed in the process.

In an alternate procedure, the mobile or flowable gel comprising the heat-softened organic polymer, the indigotin or indigotin derivative nucleating agent, the volatile organic foaming agent, *e.g.*, pentane and the organic bromide self-extinguishing agent, in the desired proportions can be extruded into a zone of lower pressure such as the atmosphere and thereafter quickly cooled, prior to appreciable expansion of the extruded material, to a temperature of about 40°C. or below to harden or solidify the extruded polymeric material containing the volatile organic foaming agent, the nucleating agent and the organic bromide flame-proofing agent uniformly dispersed throughout, and thereafter crushing or grinding the cooled product to produce latent foaming granules of the polymeric resin. The mobile gel can be extruded as a plurality of strands as a sheet, ribbon, or bar or it can be cut into globules as it is extruded, and rapidly cooled to produce the latent foaming granular product containing the ingredients uniformly dispersed throughout. Such latent foaming granules are capable of being foamed, *e.g.*, by heating in a porous mold, to form self-extinguishing cellular bodies or articles having uniform fine cells and a shape conforming to that of the mold. In all such methods for making the self-extinguishing or non-self-extinguishing latent foaming granular material, it is advantageous to employ as the foaming agent those volatile organic compounds which are normally liquid at room temperature or thereabout and atmospheric pressure.

Example 1

(A) Polystyrene having a viscosity characteristic of 22 centipoises (determined for a 10 weight per cent. solution of the polystyrene in toluene at 25°C.) was fed to a 6·4 cm diameter screw type plastics extruder at a rate of 13·5 kg per hour. The polystyrene was pressed

and heated at temperatures between 160° and 180°C. in a first section of the barrel of the extruder, then was mixed with methyl chloride fed under pressure to a second section of the barrel of the extruder at a rate of 1·35 kg per hour. The materials were mixed, cooled and forwarded under pressure in the second section of the extruder and fed at a temperature of about 160°C. into a blender-cooler. Just prior to entering the blender-cooler the stream of the polystyrene and the methyl chloride was mixed with 3 per cent. by weight of 1,1,2,2-tetrabromoethane, based on the weight of the polystyrene, which material was fed into admixture with the stream of the polystyrene and methyl chloride at a rate of 0·4 kg per hour. The resulting mixture was blended into a uniform composition in the blender-cooler under a pressure of about 42·2 kg/cm² gauge pressure and was extruded through a die into the atmosphere wherein the extruded material foamed to form a cellular body. Test pieces having the dimensions of 0·6 × 2·5 cm cross-section by 15·2 cm long were cut from the foamed product. The foam was observed for its cell size and the value was recorded. The test pieces were used to determine a flammability or self-extinguishing characteristic for the foamed product. The procedure for determining the self-extinguishing property of the foam was to hold a test piece by one end in a horizontal position with the 2·5 cm. side vertical then to move a microburner with a 2·5 cm. long flame under the free end of the test piece of the foam and ignite it, thereafter the flame is removed and the time in seconds for the ignited foam to be self-extinguished is recorded. The product prepared without the indigo compound was a foam having cells of 5 millimeters diameter. The ignited foam by test was self-extinguishing in a time of 5·3 seconds.

(B) This portion of the example illustrates the use of indigo compounds according to the invention. While continuing the feed of polystyrene and extruding of the gel containing the 1,1,2,2-tetrabromoethane to produce foam as described in part A above, there was fed to the extruder 0·25 per cent. by weight of indigotin powder, together with the granular polystyrene. The product was examined for cell size and tested for self-extinguishing characteristics as described above. The product was composed of uniform fine cells of 0·5 millimeter diameter, and when ignited was self-extinguishing in one second.

(C) This portion of the example illustrates, for purpose of comparison, the employing of a silicon-containing nucleating agent. While continuing the feed of polystyrene and extruding of the gel containing the 1,1,2,2-tetrachloroethane to produce foam as described in part A above, there was fed to the extruder 0·5 per cent. by weight of finely divided hydrated calcium silicate as nucleating agent for decreasing the size of the cells in the foamed product. The product was examined for cell size and tested for self-extinguishing properties. The product was composed of uniform fine cells of 1·3 millimeters diameter, and was self-extinguishing in 18 seconds when ignited. The results of the experiments are summarized in Table I:

TABLE I

Test No.	Additive Kind	Additive %	Foamed Product Cell Size mm.	Self-Extinguishing Time Sec.
A	None	—	5	5.3
B	Indigotin	0.25	0.5	1.0
C	Silene EF	0.5	1.3	18.0

Example 2

Part B of Example 1 was repeated varying the amount of indigo compound between 0·07 to 0·3 per cent by weight. Table II gives the cell size and self-extinguishing characteristics of the foamed product.

TABLE II

Run No.	Foamed Product Indigotin %	Cell Size mm.	Self-Extinguishing Time Sec.
1	0.07	1.7	1.4
2	0.15	1.0	—
3	0.3	0.5	1.0

In a similar manner as described in Part B of Example 1, foamed products were produced, however, varying the amount of the flame-proofing agent. Table III gives the cell size of the foamed product thus obtained and its self-extinguishing time in seconds.

TABLE III

Run No.	Self-Extinguishing Agent Indigotin	1,1,2,2-Tetrabromo-ethane	Foamed Product Cell Size mm.	Self-Extinguishing Time Sec.
1	0.15	1.0	0.83	5.5
2	0.15	1.5	0.93	3.1
3	0.15	2.0	0.97	2.1
4	0.15	2.5	0.97	1.5

We claim:

1. Cellular foamed alkenyl aromatic resin product which is made flame-retardant or self-extinguishing by a content of a flame-proofing agent, characterized in that it contains as a synergist an indigo compound.

2. The product of Claim 1 in which the indigo compound is indigotin white, a derivative thereof, or a thioindigotin compound having the general formula of the accompanying drawings, wherein R represents a radical of the group consisting of the -NH and -S- radicals, X and Y each represents a member of the group consisting of hydrogen, halogen, and lower alkyl radicals containing from 1 to 4 carbon atoms and Z is a member of the group consisting of hydrogen, halogen, and the sulfonate radical of the formula $-SO_3M$ wherein M is an alkali metal.

3. The product of Claim 1 or 2 in which the synergist is indigotin, 5,5',7,7'-tetrabromo indigotin and/or 6,6'-dichloro-4,4'-dimethyl thioindigotin.

4. The product of any of Claims 1 to 3 in which the indigo compound is present in a proportion ranging from 0·001 to 3 per cent. by weight based on the weight of the polymer.

5. The product of any of Claims 1 to 4 in which the flame-proofing agent is an organic bromine-containing compound which contains a number of bromine atoms attached to carbon atoms in an aliphatic or cycloaliphatic ring.

6. The product of Claim 5 in which the organic compound contains at least 45 per cent. by weight of bromine.

7. The cellular foamed alkenyl aromatic resin product substantially as herein before defined with reference to the foregoing Examples.

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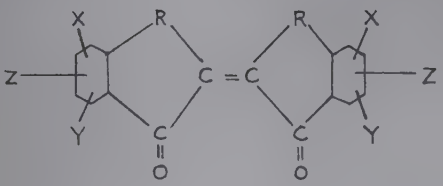
Agent for the Applicants.

Dated this 23rd day of December 1960.

MGIP Santh.—SL—106 Patent/62—15-7-63—100.

THE DOW CHEMICAL COMPANY.
NO. 74652 of 1960.

(1 Sheet)



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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74654, 23rd December 1960/2 Paus 1882 (Saka). (Accepted 5th June 1962.)

PRODUCTION OF POLYFORMALDEHYDES.

HOUILLERES DU BASSIN DU NORD ET DU PAS-DE-CALAIS, OF 16, PLACE SAINT-AMÉ, DOUAI (NORD), FRANCE, A FRENCH COMPANY.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to the production of polyformaldehyde, and more particularly to the production of polyformaldehyde by subjecting formaldehyde, in the absence of a catalyst, to ionising radiation at a temperature below —60°C.

We have found that at temperatures below —60°C., a whole series of temperature zones can be distinguished in which the conditions most favourable for polymerisation by irradiation differ substantially.

In the first place, —118°C. is the melting point of formaldehyde monomer so that above this temperature the reaction takes place in the liquid phase, whereas below this temperature it is effected in the solid phase.

At temperatures above —118°C., but below —60°C., the temperature range of from —118°C. to —80°C. is preferably used, because above —80°C. the spontaneous thermal polymerisation of formaldehyde is too brisk and the reaction cannot be effectively controlled. In the range of —118°C. to —80°C., this spontaneous thermal polymerisation is relatively slight although it is detectable.

According to one feature of the present invention, therefore, the irradiation polymerisation of formaldehyde is carried out at a temperature of from —118°C. to —80°C., the formaldehyde monomer being in the liquid form.

In this case a polyformaldehyde is formed which is translucent and compact. It is somewhat difficult to eliminate the residual monomer from this polymer so that it is often advantageous to dilute the liquid formaldehyde monomer with an inert, non-polymerisable, liquid diluent, such as a hydrocarbon or an organic oxide for example hexane or diethyl ether, at the rate, for example, of from 50% to 80% by weight, the polymer then being obtained in powdered form.

At temperatures below —118°C., it has been found that there is a relatively narrow temperature zone, in the region of —160°C., on each side of which the reaction takes place with a distinctly different character.

Thus, between about —160°C. and —118°C. irradiation of the solid monomer gives rise to a polymer which, on being heated, does not appear to undergo any polymer chain growth, that is formation of the polymer is substantially or wholly completed during irradiation.

According to another feature of the invention, therefore, solid formaldehyde monomer is subjected to ionising radiation, in the absence of any diluent, at a temperature of from about —160°C. to about —118°C.

On the other hand, below about —160°C. that is to say approximately between —196°C. and —160°C., the irradiated monomer, when it is heated, tends to give rise to an explosive reaction which, it is thought, may be due to the accumulation of active low temperature centres and the abrupt spontaneous polymer chain growth from these active centres on heating.

We have found that it is possible to overcome this disadvantage by effecting irradiation of the monomer at temperatures of from about —196°C. to about —160°C in the presence of a moderating agent which reduces the extent of heat liberation due to polymer chain growth when the reaction mass is heated to temperatures above —160°C.

Suitable moderating agents are inert, non-polymerisable, diluents, such as hydrocarbons, *e.g.* hexane, and organic oxides, *e.g.* diethyl ether. It is also possible to use the polymer, that is polyformaldehyde, itself as the moderating agent. When diluents such as the above are used they are preferably present in an amount of from 20 to 50% by weight of the mixture; if the monomer were diluted by more than 50% the yield of polymer would be undesirably reduced.

When polyformaldehyde is used as the moderating agent it is preferably formed *in situ* by subjecting formaldehyde monomer to relatively weak ionising radiation, in the absence of any diluent, at a temperature of from about —196°C. to about —160°C. then heating the reaction mass to about —80°C. so to permit polymer chain growth from the relatively limited number of active centres formed by the first irradiation, then cooling the reaction mass to a temperature of from —196°C. to —160°C. and again subjecting it to irradiation, the polymer previously formed then acting as the moderating agent.

According to a still further feature of the invention, therefore, polyformaldehyde is formed by subjecting formaldehyde monomer to ionising radiation, in the absence of any diluent, at a temperature of from —196°C. to —160°C., the total radiation dose being not more than 360 Roentgens, heating the reaction mass to —80°C. then cooling the reaction mass to a temperature from —196°C. to —160°C. and subjecting it to further ionising radiation, the total radiation dose being at least 100 Roentgens, and preferably at least 500 Roentgens. Advantageously the latter steps of heating the reaction mass, cooling the reaction mass, and subjecting the cooled reaction mass to further irradiation are repeated until the desired yield of polymer is obtained.

The processes in which a moderating agent is employed are interesting, but the preferred method according to the invention is that which involves irradiation in the absence of any diluent at a temperature of from —160°C. to —118°C. In this case, the preferred conditions of irradiation are a radiation dose of the order of 1000 Roentgens at a temperature of about —130°C.

It should be noted that the temperatures referred to above correspond to the following phenomena:

—196°C: temperature of liquid nitrogen;
—160°C: melting point of isopentane;
—130°C: melting point of pentane;
—118°C: melting point of formaldehyde monomer;
—80°C: temperature of "dry ice".

Nevertheless, the temperatures referred to above in connection with formaldehyde polymerisation phenomena are relatively approximate because the phenomena to which reference has been made develop fairly progressively with the temperature so that the temperature limits indicated should each be regarded as estimated to approximately plus or minus 5°C.

In order that the invention may be more fully understood, the following examples are given by way of illustration only:

EXAMPLE 1

Liquid formaldehyde monomer was subjected to varying doses of radiation at a temperature of about —80°C., in the absence of a diluent. The irradiation was effected with a source of cobalt 60 having an intensity of 13 Roentgens a minute.

In a first experiment, the period of irradiation was 30 minutes, that is to say the total dose was 400 Roentgens.

In a second experiment, the period of irradiation was 60 minutes, that is to say the total dose was 800 Roentgens.

Finally, in a third experiment, the period of irradiation was 15 hours 30 minutes, that is to say the total dose was 12,000 Roentgens.

In these three experiments, the percentage of polymer formed in relation to the formaldehyde initially present was respectively: 10%, 30% and 100%. The polymer was obtained in the form of a white translucent mass.

When the irradiation was continued up to a total dose of 14,500 Roentgens, the yield was 100% and the product obtained had a melting point of 180+1°C. and an intrinsic viscosity of 1.7.

EXAMPLE 2

The third experiment of Example 1 was repeated, that is to say using a total dose of 12,000 Roentgens, but the

pure formaldehyde monomer was replaced by a solution containing 50% by weight of formaldehyde monomer and 50% by weight of diethyl ether. A 44% yield of polymer was obtained, the polymer being in granular form.

Example 3

Solid formaldehyde monomer was subjected to varying doses of radiation at temperature of about —130°C. in the absence of a diluent. The experiments were carried out with the same source and the same intensity as in Example 1. In three successive experiments, the periods of irradiation were respectively; 15, 30 and 45 minutes, corresponding to doses of 200, 400 and 600 Roentgens. A yield of 15, 20 and 23% of polymer was obtained respectively in relation to the monomer used.

The polymer thus obtained was formed in the actual course of the irradiation. After elimination of the residual monomer, a fibrous product was obtained consisting of needles of crystalline appearance; this product could be readily broken into fragments.

Example 4

A 30% solution of formaldehyde monomer in diethyl ether was irradiated for one hour by means of a source of cobalt 60 having an intensity of 13 R/minute (that is to say a total dose of 780 Roentgens) at —130°C. At this temperature, the solution was liquid. A 15% yield of polymer was obtained.

Example 5

Solid formaldehyde monomer was subjected to irradiation at —186°C. in the absence of any diluent. It was found that with a low intensity radiation, that is with an intensity of the order of 13 Roentgens per minute as in the previous example, no apparent polymerisation was observed but that, after irradiation, polymerisation occurred when the reaction mass was heated, beginning at about —165°C. Thus in a series of experiments with a source having an intensity of 13 Roentgens per minute, formaldehyde was subjected to periods of irradiation of: 5, 15, 30, 60, 120 minutes and 10 hours 30 minutes, corresponding to respective doses of 65, 200, 400, 800, 1600 and 8300 Roentgens. Yields of: 11, 5, 27, 38. 42, 63 and 100% by weight respectively of products having a crystalline appearance and satisfactory physical characteristics were obtained. Thus the product obtained with a dose of 200 Roentgens had an intrinsic viscosity of 3.8, while the product obtained with a dose of 8300 Roentgens had an intrinsic viscosity of 2.4.

In every case, the product had the same melting point, namely 180±1°C.

On the other hand, with much higher intensities of the order of 1500 Roentgens per minute, polymerisation was effected in the actual course of the irradiation at —196°C. Thus with such an intensity, a yield of 100% was obtained after 30 minutes of irradiation, that is to say a total dose of 45.000 Roentgens. With this level of radiation intensity, the reaction was, however, somewhat violent and difficult to control.

Example 6

A mixture of 37% by weight of diethyl ether and 63% by weight of formaldehyde monomer was irradiated for one hour with a source having an intensity of 13 Roentgens per minute at —196°C.; the total dose received was thus 780 Roentgens. The yield of polymer obtained was 15.5%.

This example, like Examples 2 and 4 above, shows that the yield of polymer is reduced by nearly a half, other things being equal, by the presence of the diluent. This lower yield may be compensated for by effecting irradiation for longer periods or by using higher intensities of radiation in order to increase the total dose applied.

Example 7

Solid formaldehyde monomer was irradiated with a total dose of about 900 Roentgens in the absence of any diluent at a temperature of —196°C. to give a polymer yield of 32%. The reaction mass was heated from —196°C. to —80°C. and was then cooled again to —196°C. and was subjected to a further dose of 400 Roentgens to give an additional polymer yield of 8%. In another run the second irradiation was carried out to give a total dose of 870 Roentgens which gave an additional polymer yield of 14%.

Successive heating, cooling and irradiation can be repeated until the desired yield of polymer is obtained.

We claim:

1. A process for the production of polyformaldehyde which comprises subjecting liquid formaldehyde monomer to ionising radiation at a temperature of from —118°C. to —80°C.

2. A process according to Claim 1, in which the formaldehyde monomer is diluted with an inert, non-polymerisable, liquid diluent.

3. A process according to Claim 2, in which the mixture of monomer and diluent contains from 50 to 80% by weight of diluent.

4. A process according to Claim 2 or 3, in which the diluent is a hydrocarbon, such as hexane, or an organic oxide, such as diethyl ether.

5. A process for the production of polyformaldehyde which comprises subjecting solid formaldehyde monomer, in the absence of any diluent, to ionising radiation at a temperature of from —160°C. to —118°C.

6. A process according to Claim 5, in which irradiation is carried out at a temperature of about —130°C.

7. A process according to Claim 5 or 6, in which the total radiation dose is of the order of 1000 Roentgens.

8. A process for the production of polyformaldehyde which comprises subjecting formaldehyde monomer to ionising radiation at a temperature of from —196°C. to —160°C. the monomer being in admixture with a moderating agent which reduces the extent of heat liberation due to polymer chain growth when the reaction mass is heated to temperatures above —160°C.

9. A process according to Claim 8, in which the moderating agent is an inert non-polymerisable diluent and constitutes from 20 to 50% by weight of the reaction mass.

10. A process according to Claim 9, in which the diluent is a hydrocarbon, such as hexane, or an organic oxide, such as diethyl ether.

11. A process according to Claim 8, in which the moderating agent is polyformaldehyde.

12. A process according to Claim 8, in which formaldehyde monomer is subjected to ionising radiation, in the absence of any diluent, at a temperature of from —196°C. to —160°C. the total dose of radiation being not more than 300 Roentgens, the reaction mass is heated to —80°C. and then cooled to a temperature of from —196°C. to —160°C. and is then subjected to further ionising radiation, the total dose of radiation being at least 100 Roentgens.

13. A process according to Claim 12, in which the total radiation dose for the second irradiation is at least 500 Roentgens.

14. A process according to Claim 12 or 13, in which the steps of heating the reaction mass to —80°C., cooling the reaction mass to a temperature of —196°C. to —160°C. and further irradiating the reaction mass, are repeated until the desired yield of polymer is obtained.

15. A process for the production of polyformaldehyde substantially as herein described with reference to any of the Examples.

16. Polyformaldehyde when produced by the process claimed in any of the preceding Claims.

R. HALL,

OF REMFRY & SON,

Agent for the Applicants,

Dated this 23rd day of December, 1960.

MGIP Santh.—81—105 Patent/62—27-6-63—100.

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74655, filed 23rd December 1960, 2nd Paus 1882 (Saka.)
(Accepted 24th May 1962.)

IMPROVEMENTS IN OR RELATING TO CONTAINER HAVING TWO NESTABLE MEMBERS.

FRANK WYATT LAWSON, A CITIZEN OF THE UNITED STATES OF AMERICA, OF 114 JEFFERSON ROAD, PRINCETON, NEW JERSEY, UNITED STATES OF AMERICA, ENGINEER.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to a container comprising two nestable members capable of interconnection to form a closed chamber, suitable for storing and transporting a large variety of commodities.

One of the uses contemplated is the storage and shipment of asphalt which has posed quite a problem over the years. The shipment of asphalt in cylindrical drums involves discarding the drums after they have been emptied, or at relatively high expense shipping them back to the source to be refilled. Moreover, the handling of such drums and stacking them for storage and shipment has been costly and time consuming.

Similar problems are encountered in the storage and shipment of many other products, and in the case of fluid materials, inadequate provisions have been made in the past for their introduction and removal with respect to conventional containers.

It is among the objects of the present invention to provide a container comprising two nestable members each of substantially polygonal cross-section and each having side walls diverging from a closed base to a relatively larger open base, the open bases providing complementary surfaces for effecting a joint, and one of the members providing a surface for cooperation with a handling implement. The two members are of substantially equal size and each open base is preferably provided with a peripheral flange on which the complementary surfaces are formed. Clamping means for engaging the flanges will assure retention of the members in assembled relationship until such time as their disassembly is desired. The closed base of one of the members preferably contains a filling opening to which a removable closure is applied so as to lie below the limiting plane of the outer surface of the base, and the other of the members is preferably provided with a discharge opening remote from the center thereof and contains a removable closure lying within planes circumscribing such member.

The two members are preferably formed primarily from sheet metal, for which purpose sheet aluminum has been found to be eminently satisfactory, and the closed bases are indented by pressing or otherwise so as to be substantially complementary. The closed bases preferably provide external grooves for cooperation with handling means such as the forks of a lift truck, cables, bands, or the like, and preferably a plurality of such external grooves are provided in each of the closed bases. The closed base of each member preferably has an area exceeding that of any of its side walls to provide, among other advantages, stability in handling, shipping and storage, and a proper heat balance where the containers are composed of metal, to facilitate the heating of the contents of such containers when used for the storage and shipment of thermoplastic materials such as asphalt. Each of the members preferably has a substantially rectangular cross-section which may be square. Each member of the container is substantially a frustum of a pyramid whose elements are only slightly inclined to the vertical so as to provide a high degree of spatial efficiency, approaching that defined by a prism. One of the members is provided with lifting eyes which lie within the circumscribing planes so as not to preclude nesting. The lifting eyes are preferably pivotally mounted adjacent corners of the larger base of such member. One of the closed bases is preferably provided with external skids projecting beyond the other portions of the base and the other member preferably has indentations formed externally thereof to receive the skids when the containers are attacked, thus providing interfitting elements tending to retain the stacked containers in their relative positions during storage and shipment. The skids are preferably externally convex to some degree to facilitate sliding.

Accordingly, the present invention provides a container comprising two nestable members each of substantially polygonal cross-section and each having side walls diverging from a closed base to a relatively larger open base, said members having supporting means relieving said side walls of load under nested conditions, said open bases providing complementary surfaces for effecting a joint, and one of said members providing a surface for cooperation with a handling implement.

A more complete understanding of the invention will follow from a description of the accompanying drawings wherein:

Figure 1 is a perspective view of an assembled container conforming to the present invention;

Figure 2 is a sectional elevation taken along line 2-2 of Figure 1;

Figure 3 is a fragmentay sectional elevation on an enlarged scale depicting a joint between the two members defining the container;

Figure 4 is a side elevation depicting two of the assembled containers in stacked relationship;

Figure 5 is a fragmentary sectional elevation depicting several of the members in nested relationship;

Figure 6 is a bottom plan view on a reduced scale of one of the containers; and

Figure 7 is a fragmentary sectional elevation of a discharge fitting and a cooperating tap.

The container 10 is composed of an upper member 12 and a lower member 14 having closed bases 16 and 18 respectively, and open bases provided with, peripheral flanges 20 and 22 respectively. These flanges are integral with the respective members and may be attached by welding or formed by upsetting. The flange 20 diverges outwardly to define a bell 24 which receives a cooperating outwardly convergent spigot 26 provided by the flange 22. By virtue of the interfitting bell and spigot, the joint between the upper and lower members can be rendered as fluid tight as the contents require. As a matter of fact, as illustrated in Figure 3, a deformable packing 25 is interposed between the members to produce a seal which will be completely fluid tight.

The two members constituting the container are maintained in assembled relationship by means of a plurality of clips 28 bridging the two flanges at desired intervals. Each clip comprises a threaded bolt member 27 and a sleeve member 29. These members are provided with ends 30 and 31 respectively bent to hooked form so as to extend into channels 32 formed in the surfaces of the flanges remote from their interfitting ends. The threaded ends 33 of the bolt members 27 receive nuts 35 to adjust the clips during assembly and disassembly operations.

The closed base of each of the members 12 and 14 is formed with intersecting external grooves 34 arranged to receive a pair of forks of a conventional lift truck introduced from any of the four sides of the container. The grooves 34 constituting one pair are parallel to one another and perpendicular to the parallel grooves constituting the other pair. Each of the closed bases 16 and 18 is provided with external corner pads 36, edge pads 38, and a central pad 40 lying in a limiting plane corresponding with the outermost portion of the major surface. In the case of the upper member 12, each corner pad 36 contains an indentation or depression 42

intended to receive a skid or foot 44 projecting beyond the plane of the major surface of the closed base of the lower member 14. The central pad 40 of the closed base 16 of the upper member receives a fitting 46 having internal threads for cooperation with the external threads of a closure plug 48 providing lugs 50 for engagement by a suitable wrench for application and removal of the closure.

The central pad 40 of the closed base 18 of the lower member is also provided with a skid or foot 52 similar to those provided on its corner pads, for reception, under stacked conditions in the depressed portion of the closure 48 of the container below it.

It will be noted that the peripheral flanges 20 and 22 provide beveled corners, the flange 22 of the lower member 14 being formed with a pair of lugs 54 at each such corner supporting a pin 56 on which a lifting eye 58 is pivoted. These lifting eyes are adapted to receive cables or cable fittings of conventional types for raising and lowering the containers during the moving operations customarily encountered in the storing and shipping of materials. Reference to Figure 6 will show clearly that these lugs and lifting eyes lie within the planes which circumscribe the peripheral flanges in such a way as to permit nesting of the members as effectively as though such lifting eyes were not present.

The manner of nesting the members is clearly shown in Figure 5 from which it will be observed that the principal support of one member relative to the next is through the peripheral flanges, thereby relieving the thinner portions of the containers from such stresses as would be apt to deform them and providing sufficient lateral and vertical spacing between the nested members to assure their ready separation when desired.

Each of the lower members 14 has one of its lower corners provided with a fitting 60, having internal threads 61 to receive the external threads 63 of a plug 62 also provided with internal threads 65. With this arrangement, when the container arrives at its destination, where its contents is fluid, by displacement of the plug 62, such fluid material can be drained into the area or receptacle intended to receive it. As shown in Figure 7 a threaded tap 66 is provided with a reduced threaded end 68 complementing the threads 65 of the plug 62 and a larger threaded portion 70 complementing the threads 61 of the fitting 60. Insertion of the tap 66 followed by rotation will cause the plug 62 to advance into the container until the ports 72 of the tap communicate with the container, continued rotation establishing a fluid tight joint between the fitting 60 and a gasket 74 carried by a flange 76 on the tap 66. The location of the discharge fitting 60 at the corner is particularly advantageous where a thermoplastic material is to be discharged from the container since heat can be applied directly to the bottom of the container without danger of the flame reaching the material discharging or damaging the outlet fitting. This is particularly important in connection with flammable materials such as asphalt. Moreover, this corner location of the discharge fitting permits maximum drainage of the contents by tilting the container.

The area of the closed base 18 is shown as appreciably greater than any one of the side walls 64 of the lower member 14 so as to provide good stability to the container for handling, shipping and storage and to provide a relatively large heat transfer surface to permit rapid heating from an external source.

I claim:

1. A container comprising two nestable members each of substantially polygonal cross-section and each having side walls diverging from a closed base to a relatively larger open base, said members having supporting means relieving said side walls of load under nested conditions, said open bases providing complementary surfaces for effecting a joint, and one of said members providing a surface for cooperation with a handling implement.

2. A container as set forth in Claim 1 wherein said members are of substantially equal size.

3. A container as set forth in Claims 1 and 2 wherein each open base is provided with a peripheral flange.

4. A container as set forth in Claim 3 including clamping means engaging said flanges.

5. A container as set forth in any of the preceding claims wherein one of said closed bases contains a filling opening, and a removable closure is applied to said opening.

6. A container as set forth in any of the preceding claims wherein said members are formed from sheet metal.

7. A container as set forth in any of the preceding claims wherein said members are formed from sheet aluminum.

8. A container as set forth in any of the preceding claims wherein said closed bases are indented and substantially complementary.

9. A container as set forth in any of the preceding claims wherein said open bases are provided with peripheral flanges having interfitting surfaces.

10. A container as set forth in any of the preceding claims wherein one of said members is provided with a discharge opening at a corner defined by a pair of side walls and a closed base.

11. A container as set forth in any of the preceding claims wherein one of said closed bases provides an external groove for cooperation with a handling implement.

12. A container as set forth in any of the preceding claims wherein one of said closed bases provides a plurality of external grooves for cooperation with a handling implement.

13. A container as set forth in any of the preceding claims wherein the closed base of each member has an area exceeding that of any of its side walls.

14. A container as set forth in any of the preceding claims wherein each of said members is substantially rectangular in cross-section.

15. A container as set forth in any of the preceding claims wherein each of said members is substantially square in cross-section.

16. A container as set forth in any of the preceding claims wherein one of said members is provided with lifting eyes.

17. A container as set forth in Claim 16 wherein said lifting eyes are located at adjacent corners of the larger base of said member.

18. A container as set forth in any of the preceding claims wherein one of said closed bases is externally provided with skids.

19. A container as set forth in Claim 18 wherein said skids are externally convex.

20. A container as set forth in any of the preceding claims wherein each of said members is substantially a frustum of a pyramid.

21. A container substantially as hereinbefore described with reference to the accompanying drawing.

R. HALL

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Agent for the Applicant.

Dated this 23rd day of December 1960.

M&IPC—L—104 Patent/62—30.3.63—100.

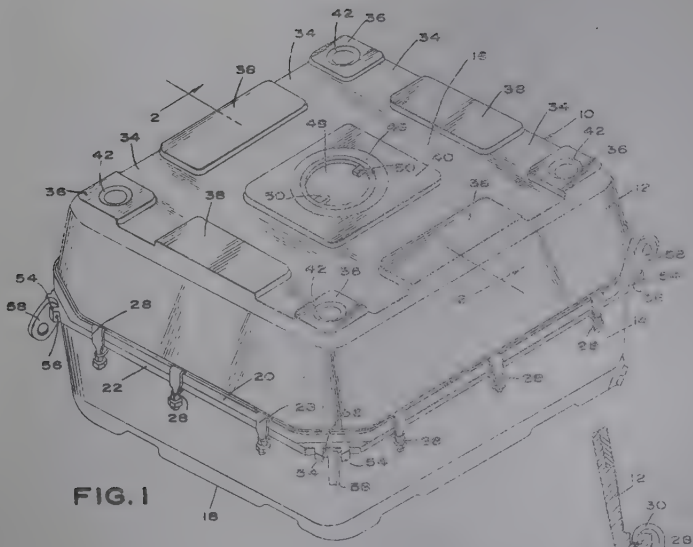

FIG. 1

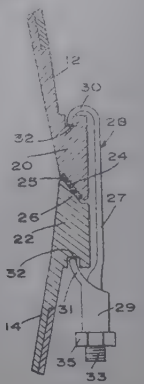

FIG. 3

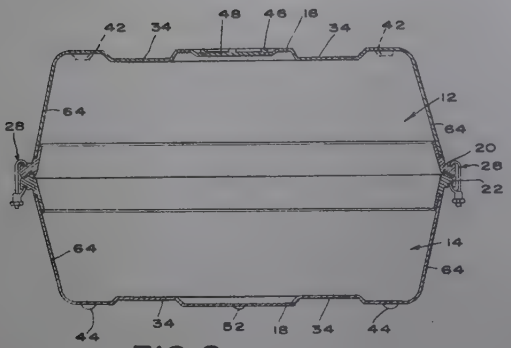

FIG. 2

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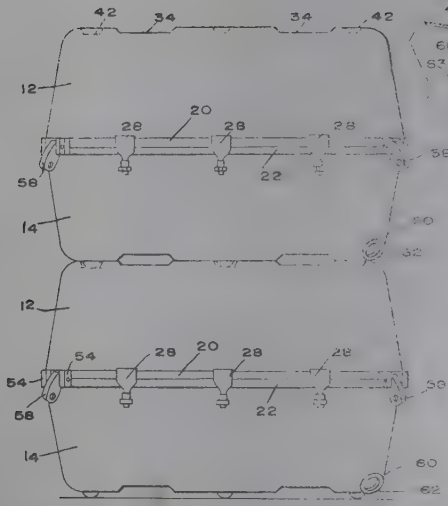

FIG. 4

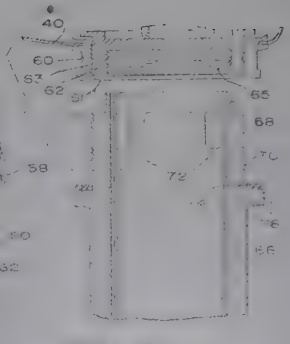

FIG. 7

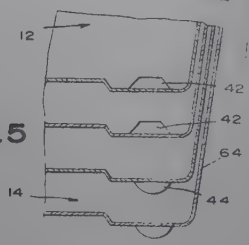

FIG. 5

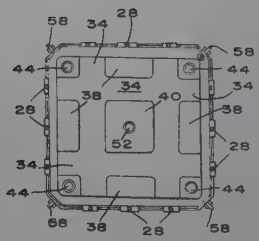

FIG. 6

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For INSPETCION CENTRE

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74656, filed 23rd December 1960./2 Paus. 1882 (Saka)

(Accepted 6th June 1962.)

"IMPROVEMENTS IN AND RELATING TO LOUDSPEAKER MEMBRANES FROM IMPREGNATED TEXTILE FABRIC AND METHODS OF MANUFACTURING SUCH MEMBRANES."

N. V. PHILIPS' GLOEILAMPENFABRIEKEN, A LIMITED LIABILITY COMPANY ORGAINZED AND ESTABLISHED UNDER THE LAWS OF THE KINGDOM OF THE NETHERLANDS, CARRYING ON BUSINESS AS MANUFACTURERS AT EMMASINGEL 29, EINDHOVEN, HOLLAND.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This invention relates to loudspeaker membranes comprising an impregnated textile fabric pressed to the desired shape and to a method of manufacturing such membranes.

Loudspeaker membranes are practically exclusively manufactured from paper fibres. The method followed requires great investments and experience. The reject percentage is high, also when allowing great tolerances in the most important accoustic quantities. The acoustic properties are not ideal, while a paper membrane is sensitive to moisture, not resistant against insect and micro-organisms and mechanically is not strong.

In spite of these drawbacks and difficulties, a product is obtained in practice from paper fibres only which can be used for the end in view.

It is true, it has been suggested to use impregnated paper of fabric as an acoustic membrane and to press this to the desired shape. However, this suggestion has not resulted in a product which can be used in practice to replace paper membranes, which is due on the one hand to the fact that cellulose lacquers cannot impose sufficient stiffness and elasticity on the membrane and on the othor hand by the fact that the difference in stiffness which should exist between the sound-radiating part and the edge for the attachment has been insufficiently taken into account.

The object of the present invention is to provide a loudspeaker membrane, the acoustic properties of which are at least comparable to those of the best paper membranes.

According to the invention, such a membrane consists of an impregnated textile fabric which is pressed to the desired shape, in which the whole is stiffened with a stiffening agent and which is characterized in that the sound-radiating part is coated with a synthetic, thermo-hardenable, softening agent free lacquer and in which the edge part may be impregnated with a plastic mass.

For the manufacture of such a membrane, preferably the following method is used. The textile fabric is impregnated with a stiffening agent, the stiffening agent and the quantity being chosen so that after pressing to the desired shape and after impregnation, if any, of the edge with a plastic mass, the whole is sufficiently elastically deformable, as required for the edge part of a loudspeaker membrane, after which the sound-radiating part, after passing to obtain the stiffness required, is coated with a synthetic, thermo-hardenable, softening agent free lacquer.

A stiffening agent is understood to mean in this connection an agent which, by chemical or physical converaion, imposes non-deformability on the fabric during or after the shaping.

As stiffening agents may be used, for example, thermohardenable or thermoplastic synthetic or natural products such as urea and phenol resins, colophony, starch and the like. By textile fabric are also understood in this connection the fabrics of the textile fabric structure.

The fabrics may be obtained for example from cotton, natural silk and rayon, nylon, polyester fibre and the like.

Preferably, the fabric should have a weight not exceeding 70 g per m^2 in connection with the ultimate weight of the membrane.

From acoustic considerations, for example a conical membrane having a diameter of 15 cms of the base and an special angle of 120° coated with lacquer may not exceed the weight of 3 g.

Acoustically satisfactory membranes can be obtained in particular by coating the membrane with a synthetic, thermohardenable, softening agent-free lacquer which meets definite mechanical requirements which are also imposed on so-called "wound wire" lacquers.

Wound wire lacquers are lacquers which are used for coating metals, electric conductors in wire form, destined for winding coils for transformers, motors and the like. These lacquers should have satisfactory electrically insulating properties and should in addition meet high mechanical requirements, in particular as to hardness and elasticity.

It has surprisingly been found that lacquers which meet the following mechanical requirements can be used for the non-deformable membrane, thereby imposing acoustic properties on these membranes so that these membranes can replace paper membranes in every respect.

The said mechanical requirements are in particular :

a. the hardness of the lacquer layer on a copper wire in the dry state should be at least 3 H according to DIN 46435 and DIN 46453-13.

b. copper wires having a diameter of the cross-section of at least 287μ and coated with a lacquer layer should be capable of being wound at least once on a mandril having the diameter of the wire without damaging of the lacquer layer occurring (see DIN 46453-9).

c. In the case of a sudden load up to breaking of the copper wire, a lacquer layer provided on this wire may not show any hair-cracks.

Lacquers which give layers meeting the above requirements may be composed *inter alia* on the basis of ethyline resins, polyurethane resins, polyvinyl acetals, acryl resins, polyesters, urea or phenol resins or mixtures of these resins.

The lacquers may in addition contain thermoplastic substances such as polyamides.

They may be used in the form of solutions in volatile solvents or emulsions in water.

In order that the invention may be readily carried into effect, it will now be described, by way of example, with reference to the examples and the attached drawings, in which

Fig. 1 diagrammatically shows a fabric which may be used in the method.

Fig. 2 is a sectional view of a membrane formed,

Fig. 3 is a sectional view of a membrane shown in Fig. 2 coated with a lacquer layer.

Price : TWO RUPEES.

Fig. 1 diagrammatically shows a plan view of a fabric with equal warp and woof. This fabric is impregnated, for example, with a thermohardenable resin on the basis of a novolak, for example consisting of a mixture of a novolak and hexamethylene tetramine.

The thus obtained material is then hardened while shaping, for example by pressing at elevated temperature in a mould to a non deformable membrane as shown in Fig. 2.

The thus obtained non-deformable membrane, however, in itself is not suitable for use as an acoustic membrane, In most of the cases in particular because it is not or insufficiently airtight.

In Fig. 2, the cone proper which sets the air in motion is indicated by 1, grooves serving as hinges for the moving membrane are indicated by 2.

The non-deformable membrane is coated on one or on both sides with a lacquer layer by immersing, spraying, by means of a brush or some other suitable process, while not coating the grooves 2. If desired, these grooves may be impregnated with a plastic mass, for example as is used in the case of paper membranes, after the hardening of the lacquer layer.

Fig. 3 shows a sectional view of finished membrane. The numerals 1 and 2 have the same meanings as in Fig. 2, 3 is the lacquer layer.

Example 1

A conical membrane with satisfactory acoustic properties was obtained as follows :

A cotton fabric having equal warp and woof and a weight of 40 g per m² was impregnated with a solution of a phenol novolak and hexamethylene tetramine in an ethanol-water mixture.

After drying, the impregnated fabric was transferred to a mould and heated under a pressure of approximately 2 atmospheres at 150°C for 10 seconds. For a good detachment, it is recommended to use a detaching agent or to coat the impregnated fabric after drying of the novolak with, for example, a melamine resin. The non-deformable membrane was then coated with a lacquer layer by means of a wound wire lacquer marketed by Messrs. Beck(Hamburg, Germay) under the name of "Supradurit LK 19", of which Applicants assume that it is a lacquer on a polyurethane basis. The lacquered membrane was then heated to approximately 200°C for from 2 to 5 minutes, when the lacquer hardened.

The thus obtained membrane is suitable for use in a loudspeaker.

The hardness of the lacquer measured at indicated sub a amounts to approximately 4 H.

Example 2

A lacquer was composed by preparing a 35% by weight solution in a mixture of methyl glycol acetate, toluene and ethyl acetate of the following mixture : 7 parts by weight of an ethoxyline resin, obtainable in trade as "Epikoot.1007". a product of Koninklijke Shell ; 3 parts by weight of an urea formaldehyde resin.

The lacquer was provided by means of a brush on a non-deformable membrane obtained in the same manner as in Example I. After coating. the lacquer layer was dried and the lacquered membrane was then heated in a furnace to 200°C for 10 minutes.

The membrane thus obtained has satisfactory acoustic properties.

The hardness of the lacquer measured as indicated sub a amounts to approximately 6 H.

Example 3

A lacquer was composed by dissolving 10 parts of weight of polyvinylformal and 4 parts by weight of a cresol-formaldehyde novolak in 86 parts by weight of xylene cresol 1 : 1.

The lacquer was provided on a non-deformable membrane and dried. After heating at 180°C for 15 minutes, a membrane having very good acoustic properties was obtained.

The hardness of this lacquer amounted to approximately 8 H.

The membranes manufactured according to the above examples all of them showed the following features. The membranes are resistant to attacks by insects and micro-organisms and withstand the influence of water and temperature.

Even when the lacquer layer is provided on the non-deformable membrane manually by means of a brush, the reproducibility in acoustic respect is particularly large. For example, in a series of 100 conical membranes, a reproducibility of the resonant frequency of approximately 1 c/s was obtained.

As a result of the larger mechanical strength, the membranes manufactured according to the invention may be stressed four times heavier than corresponding paper membranes.

The efficiency in the medium tone range (800-5000 c/s) in the case of membranes according to the invention is larger than in corresponding paper membranes. The sound pressure in the medium tone range in membranes according to the invention exceeds that of paper membranes by a factor up to 4.

The result is that a conical membrane according to the invention gives a very natural sound reproduction, while in addition the intermodulation in these membranes is much smaller than in the case of paper membranes.

WE CLAIM :—

1. A loudspeaker membrane comprising an impregnated textile fabric which is pressed to the desired shape, in which the whole is stiffened with a stiffening agent, characterized in that the edge for the attachment is impregnated, if desired, with a plastic mass and the sound-radiating part is coated with a synthetic, softening agent-free, thermohardenable lacquer.

2. A method of manufacturing a loudspeaker membrane as claimed in Claim 1, in which a textile fabric is impregnated with a stiffening agent, characterized in that the stiffening agent and the quantity of same are chosen so that after pressing to the desired shape and impregnation, if any, of the edge with a plastic mass, the assembly is still sufficiently elastically deformable as required for the edge part of the loudspeaker membrane and that the sound-radiating part, after pressing to obtain the required stiffness, is coated with a synthetic, thermohardenable, softening agent-free lacquer.

3. A method in Claim 2, characterized in that a deformable fabric having a weight of at most 70 g per m² is used.

4. A method as claimed in Claim 1, characterized in that a lacquer is used having satisfactory mechanical properties, such as wound wire lacquers on a basis of an ethoxyline resin, a polyurethane resin, polyvinyl acetal resin, polyesters, an acryl resin, an urea resin or phenol resin, or mixtures of these resins.

5. A method as claimed in Claim 2, characterized in that the edge part is impregnated with a plastic mass.

6. A loudspeaker provided with membranes as claimed in Claims 1 to 5.

B DePENNING
of CANTWELL & CO.,
Agent for the Applicants.

Dated this 23rd day of December 1960.

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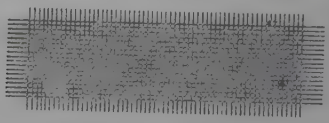

FIG. 1

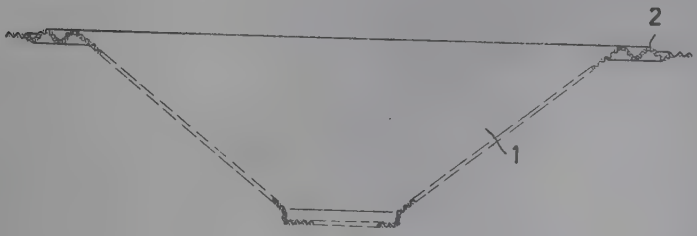

FIG. 2

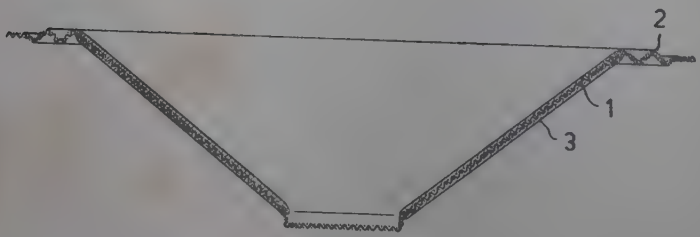

FIG. 3.

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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74657, 23rd December 1960. 2nd Paus 1882 (Saka). (Accepted 23rd June 1962.)

BASICALLY SUBSTITUTED PROPANOLS ALKENYLAMINES OBTAINABLE THEREFROM BY DEHYDRATION, ACID ADDITION SALTS THEREOF, PROCESS FOR THEIR MANUFACTURE, AND PHARMACEUTICAL PREPARATIONS CONTAINING SAME.

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The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

The present invention relates to (1) basically substituted propanols of the formula shown in Fig. 1 of the accompanying drawings, in which R represents a hydrogen atom or the methoxy group, R_1 represents a phenyl radical that may be substituted by a methoxy group, or an alkyl group containing from 1 to 4 carbon atoms, and R_2 represents a hydrogen atom or the methyl group, to (2) alkenylamines obtainable therefrom by dehydration and corresponding to the formula shown in Fig. 2 of the drawings, in which R, R_1 and R_2 have the meanings given above, to (3) physiologically compatible acid addition salts thereof and to (4) pharmaceutical preparations containing these compounds as the active ingredients.

The present invention further relates to a process for the manufacture of these compounds which comprises (a) reacting a ß-[1-phenyl-propyl-(2)-amino]-propionic acid alkyl ester of the formula shown in Fig. 3 of the drawings, in which Y represents an alkyl group containing 1-5 carbon atoms and R_2' represents a hydrogen atom, a methyl group or a benzyl group, or a ß-[1-phenyl-propyl-(2)-amino]-ethyl-phenyl-ketone of the formula shown in Fig. 4 of the drawings, in which R has the meaning given above and R_2' represents a hydrogen atom, a methyl group or a benzyl group, with organo-metallic compounds, and in case R_2' stands for benzyl, splitting off the benzyl group by means of activated hydrogen either during the reaction or following the preparation of the reaction products, or (b) reducing phenylacetone in the presence of basically substituted phenylpropanols by means of activated hydrogen, or reacting a basically substituted phenylpropanol with 1-phenyl-2-halogen-propanes, or (c) reducing by means of activated hydrogen ß-hydroxy-ß-phenyl-carboxylic acid-N-[1-phenyl-propyl-(2)]-amides of the formula shown in Fig. 5 of the drawings, in which R and R_1 have the meanings given above and R_2 represents a hydrogen atom, to form the corresponding amines, and, if desired converting the saturated basic hydroxy compounds obtained by dehydration by means of a dehydrating agent into unsaturated compounds of the formula shown in Fig. 2, in which R and R_1 have the meanings given above and R_2 represents a hydrogen atom and/or converting the compounds obtained into the corresponding salts by treatment with inorganic or organic acids.

The new products of the present invention are valuable medicaments which, in addition to being excellently tolerable, are distinguished by an excellent activity on cardiac and blood vascular circulation. Moreover, they are suitable as intermediates for the preparation of medicaments.

As starting compounds for the reaction of the basically substituted propionic acid esters with organo-metallic compounds, there enter, for example, into consideration :

ß-[1-phenyl-propyl-(2)]-amino-propionic acid methyl ester,

ß-[1-phenyl-propyl-(2)-N-methyl]-amino-propionic acid methyl ester,

ß-[1-phenyl-propyl-(2)-N-benzyl]-amino-propionic acid methyl ester,

and the corresponding ethyl esters, n-propyl esters, isopropyl esters, n-butyl esters, isobutyl esters, amyl esters, or isoamyl esters.

As organo-metallic compounds, there enter into consideration, for example, phenyl-magnesium halides such as phenyl magnesium bromide or iodide, ortho-, meta- or para-methoxyphenyl-magnesium-halides such as ortho-, meta- or para-methoxyphenyl magnesium-bromide or iodide, and lithium-phenyl or ortho-, meta- or para-methoxy-lithium-phenyl.

The reaction is advantageously carried out in the presence of a suitable inert organic solvent, for example, in the presence of an aromatic hydrocarbon such as benzene, toluene, or xylene; it is advantageous to use at least 2 mols of the organo-metalic compounds per 1 mol of the ester. After having boiled for a more or less extended period of time, the reaction mixture is decomposed by means of water, acidified and the corresponding hydroxy compound is isolated from the layer of organic solvent. By the action of the organo-metallic compounds on propionic acid esters always two equal aromatic radicals are introduced as substituents at the carbon atoms of the keto group according to the reaction scheme shown in Fig. 6 of the drawings, in which R_2 represents a hydrogen atom, a methyl group or a benzyl group.

When starting from ß-[1-phenyl-propyl-(2)-amino]-ethyl-phenylketones, i.e., from keto-compounds which already contain a phenyl radical, it is possible to introduce different substituents which correspond to the meaning indicated, at the carbon atom of the keto group.

As ß-[1-phenly-propyl-(2)-amino]-ethyl-phenyl-ketones there are suitable, for example, ß-[1-phenyl-propyl-(2)]-amino-ethyl-phenyl ketone, ß-[1-phenyl-propyl-(2)-N-methyl]-amino-ethyl-phenyl ketone, ß-[1-phenyl-propyl-(2)-N-benzyl]-amino-ethyl-phenyl ketone, and ß-[1-phenyl-propyl-(2)-N-benzyl]-amino-ethyl-(para-, meta- or ortho-methoxyphenyl) ketone. As reaction components there enter into consideration the organo-metallic compounds already cited. Furthermore, there are also suitable alkyl organo-metallic compounds containing 1-4 carbon atoms, for example methyl-, ethyl-, n-propyl-, isopropyl-, n-butyl- or isobutyl-magnesium halides, the halogen atoms being preferably bromine and iodine. The reaction is effected in the manner described for the basically substituted propionic acid esters. The above-described ß-[1-phenyl-propyl-(2')-amino]-ethyl-phenyl ketones can also be reacted with organo-lithium compounds. As reaction components there are mentioned for example : lithium phenyl and lithium n-butyl. The reaction conditions correspond to those described for the reaction with organo-magnesium compounds. The desired basically substituted propanols can be isolated by known methods from the lithium compounds so obtained for example by decomposition with water and extraction with an organic solvent.

According to another method of carrying out the process of the invention, it is also possible to reduce carboxylic acid amides of the formula shown in Fig. 5 of the drawings, wherein R and R_1 have the meanings given above, and R_2 represents hydrogen,, the reduction by means of lithium-aluminium-hydride being particularly advantageous. The carboxylic acid amides used as starting substances can be prepared, for example, by reaction of di-aryl or aryl-alkyl ketones with acetamides that carry araliphatic substituents corresponding to the meanings given above, and in which a hydrogen atom of the methylene group in α-position to the carbonyl group is replaced by lithium. These Li-N-(aralkyl)-acetamides of the formula shown in Fig. 7 of the drawings, in which R_4 represents hydrogen, can be prepared according to the method described in J. Am. Chem. Soc. 75, page 2413. They may, however, also be prepared by means of a modified Reformatsky-reaction corresponding to the method described in J. Am. Chem. Soc. 70, page 677. The amides so obtained are then advantageously reduced by means of lithium-aluminium-hydride in the presence of inert organic

Price : TWO RUPEES.

solvents such, for example, as ether, dioxane, or tetrahydrofurane. It is advantageous to add the amide to the lithium-aluminium-hydride suspension in one of the described solvents, to reflux the reaction mixture for some time, then decompose it carefully by addition of water, and working up in usual manner by separating the organic phase from inorganic components. The reduction of the carboxylic acid amides to the amides can also be effected electrolytically.

Furthermore, it is also possible to prepare the products of the present invention by reducing phenylacetone in the presence of amines of the formula shown in Fig. 8 of the drawings, wherein R and R_1 have the meanings given above. The amines which may be used as starting substances can be prepared, for example, by hydrogenation of the corresponding nitriles of the formula shown in Fig. 9 of the drawings, R and R_1 having the meanings given above.

The latter compounds are obtainable, for example, by condensation of arylketones with acetonitrile in the presence of sodamide [cf. Liebig's Annalen der Chemie, *603*, (1957), page 189].

As amines, there enter into consideration, for example :

1,1-diphenyl-1-hydroxy-3-amino-propane,
1-ortho-, meta-, or para-methoxyphenyl-1-phenyl-1-hydroxy-3-aminopropane,
3-phenyl-3-hydroxy-1-amino-pentane,
3-phenyl-3-hydroxy-1-amino-butane,
3-phenyl-3-isopropyl-3-hydroxy-1-amino-propane, and
3-phenyl-3-iso-(or sec.)-butyl-3-hydroxy-1-amino-propane.

The reduction of phenylacetone in the presence of amines is effected advantageously catalytically. As catalysts, there are used the metals of the 8th group of the Periodic System, preferably nickel catalysts, in the presence of solvents conventionally used therefore, for example water-miscible aliphatic alcohols. Noble metals such as palladium or platinum or Raney catalysts, may also be used. The reduction may also be effected by means of nascent hydrogen, for example from aluminium amalgam and alcohol, sodium amalgam, lithium-aluminium-hydride or sodium boronhydride. The reduction may also be carried out electrolytically.

Finally, the products of the present invention may also be prepared from the above-described amines by reaction with 1-phenyl-2-halogeno-propanes, chlorine, bromine or iodine coming into consideration as halogen atoms. The reaction is suitably effected in the presence of a basic compound in order to bind the hydrogen halide set free during the reaction. For this purpose, the amine to be reacted may also be used in an excess amount. As basic agents there are suitable, for example, tertiary organic bases such as trimethylamine, triethylamine, pyridine or quinoline as well as sodium-, potassium- or calcium-carbonate or -bicarbonate. The reaction can be effected with or without the use of a suitable organic solvent. As such solvents are suitable, for example, organic solvents such as alcohols, benzene, toluene, ether or chloroform. If the reaction is carried out in the presence of the above-specified organic bases, these compounds can simultaneously act as solvent and as hydrohalic acid-binding agents.

If the substituent R_2 in the formula given for the products of this invention represents a benzyl group, the benzyl radical is split off either during the reaction or following the preparation of the reaction products. This separation is advantageously effected catalytically with noble metal catalysts such as palladium. The separation of the benzyl radical is not necessary in case a hydrogenation reaction in the presence of noble metal catalysts is used for the preparation of the final products desired since the benzyl radical is separated in the reaction stage. The basically substituted propanols thus obtained can, if desired, be converted into the corresponding alkenyl amines by dehydration. The reaction is carried out in the presence of the usual dehydration agents, for example, phosphoric acid, para-toluene-sulfonic acid, phosphorus pentoxide, or acetic acid anhydride, according to the method described in Liebig's Annalen der Chemie. *603*, (1957), page 189.

The products of the present invention can be converted into the corresponding salts by means of inorganic or organic acids. As inorganic acids, there enter into consideration, for example : hydrohalic acids such as hydrochloric acid or hydrobromic acid, further sulfuric acid, phosphoric acid, and amidosulfonic acid. As organic acids, there are mentioned by way of example : formic acid, acetic acid, propionic acid, lactic acid, glycolic acid, gluconic acid, maleic acid, succinic acid, tartaric acid, benzoic acid, salicylic acid, citric acid, aceturic acid, oxyethanesulfonic acid or ethylenediamine-tetracetic acid.

The products of the present invention are valuable medicaments which are distinguished by an excellent activity on cardiac and general blood vascular circulation. For example, by infusing 1-phenyl-2-[1',1'-diphenyl-1'-hydroxy-propyl-(3')]-amino-propane-hydrochloride into an isolated rabbit's heart by the method of Langendorff at a rate of 1·2 micrograms per minute a considerable increase of the coronary blood flow was observed which reached a maximum with an administration of 2 micrograms per minute. After the infusion was discontinued, the increased blood flow was still maintained for a considerable time. Furthermore, the rate of heart-beat was reduced, and this had an influence on the whole body of the animal. The administration of small doses of this compound also caused distinct dilatation of the blood vessels in a rabbit's ear which had been isolated and perfused by the Kraskow-Pissemski method. For example, 5 micrograms of this product caused slight dilatation and 150 micrograms a very considerable dilatation of the blood vessels. The products of the present invention already cause the dilatation of the coronary and peripheral blood vessels when administered in such small doses that the toxicity (the Dos. leth. min. in mice of the above compound is 15-20 mg/kg) is practically negligible.

Similarly, when used for clinical examination, the said compound caused dilatation of the blood vessels, especially of the coronary vessels. It also caused an increased peripheral blood circulation. The dilatation of the coronary vessels occured very rapidly and, compared with the known nitro-compounds, for example, the tetra-nitric acid ester of Erythritol, this dilatation was maintained for some time (several hours). As single doses, 5-10 mg of the compound were administered.

The corresponding alkenylamines obtainable from the basically substituted propanols by dehydration also exhibit a good activity on cardiac and blood circular vascular circulation. For example, a single injection of 10 micrograms of 1-phenyl-2-[1',1'-diphenyl-propyl-(1')-ene-(3'')]-amino-propane (Example 9) caused strong dilatation of the coronary vessels. The toxicity of this compound was Dos. leth. min. i.v. in the mouse : 15 mg/kg.

The products of the invention may be applied as such or in the form of their corresponding salts, if required, in admixture with pharmaceutically suitable carrier substances either perenterally or orally. For oral administration, the preparations may be in the form of tablets or dragees which also contain the usual carriers such as lactose, starch, tragacanth or magnesium stearate, as well as the said compound as active ingredient.

The following Examples illustrate the invention but they are not intended to limit it thereto :

Example 1

1-phenyl-2-[1',1'-diphenyl-1'-hydroxy-propyl-(3')]-amino-propane.

11·4 Grams of 1,1-diphenyl-1-hydroxy-propylamine-(3) were hydrogenated with 6·7 grams of isopropanol in the presence of palladium catalyst. After the calculated amount of hydrogen had been taken up and the catalyst had been removed by filtration, the solution was concentrated under reduced pressure. 17 Grams of 1-phenyl-2-[1',1'-diphenyl-1'-hydroxy-propyl-(3')]-amino-propane in the form of an oily residue were obtained, which, after having been worked up in usual manner, gave the hydrochloride melting at 213-214°C.

The 1,1-diphenyl-1-hydroxy-propylamine-(3) used as starting material, can be prepared, for example, by the following method : ß-hydroxy-ß,ß-diphenyl-propionitrile (prepared according to the method described in Liebig's Annalen der Chemie *603*, page 194) is hydrogenated in the presence of Raney-Nickel at 80-85°C in 300 ml of methanol saturated with ammonia. After the reaction is terminated, the solution is filtered, concentrated, and the residue is dissolved in dilute hydrochloric acid and filtered with the addition of charcoal. Upon addition of 2N-sodium hydroxide solution, 1,1-diphenyl-1-hydroxy-propyl-amine-(3) melting at 143-144°C precipitates in crystalline form.

Example 2

1-phenyl-2-[1'-meta-methoxyphenyl-1'-phenyl-1'-hydroxy-propyl-(3')]-amino-propane.

12·5 Grams of ß-(meta-methoxyphenyl-ß-phenyl-ß-hydroxy-propylamine were hydrogenated with 6·7 grams of phenyl-acetone according to the method described in Example 1. After working up, there were obtained 16 grams of 1-phenyl-2-[1'-meta-methoxy-phenyl-1'-phenyl-1'-hydroxy-propyl-(3')]-amino-propane-hydrochloride, which was found to melt at 175-176°C.

The ß-(meta-methoxyphenyl)-ß-phenyl-ß-hydroxy-propylamine used as starting substance can also be prepared, as described in Example 1, by hydrogenation of ß-(meta-methoxyphenyl)-ß-phenyl-ß-hydroxy-propionitrile. The latter compound may be prepared according to the method described in Liebig's Annalen der Chemie *603*, page 194, from meta-methoxybenzophenone and acetonitrile. The product melts at 61-62°C.

Example 3

1-pheyl-2-[3'-phenyl-3'-hydroxy-pentyl-(1')]-amino-propane.

17·9 Grams of 3-phenyl-3-hydroxy-1-amino-pentane and 13·4 grams of phenylactone were hydrogenated according to the method described in Example 1. There were obtained 16·9 Grams of 1-phenyl-2-[3'-phenyl-3'-hydroxy-pentyl-(1')]-amino-propane melting at 93-95°C. The hydrochloride of the base was found to melt at 161-163°C.

3-Phenyl-3-hydroxy-1-amino-pentane used as starting material, can be prepared, for example, by hydrogenation of ß-phenyl-ß-hydroxy-valeronitrile, which has a melting point of 59-60°C. The latter compound may be obtained according to the method described in Leibig's Annalen der Chemie *603*, page 194, from propiophenone and acetonitrile. The hydrogenation is effected in the manner described in Example 1.

Example 4

1-phenyl-2-[1', 1'-diphenyl-1'-hydroxy-propyl-(3')]-amino-propane.

32·5 Grams of ß-[N-benzyl-N-(1-phenyl-propyl-(2)]-amino-propionic acid ethyl ester, prepared from ß-chloro-propionic acid ethyl ester and N-benzyl-N-(1-phenyl-propyl-(2))-amine, were added dropwise to a solution of magnesium-phenyl bromide prepared from 10 grams of magnesium and 60 grams of bromobenzene in 150 cc of ether. The reaction mixture was then refluxed for some hours. The mixture was then poured onto ice and acidified with dilute hydrochloric acid, which caused 1-phenyl-2-[N-benzyl-N-(1',1'-diphenyl-1'-hydroxy-propyl-(3')]-amino-propane-hydrochloride to precipitate. The yield was 24 grams.

(b) The benzyl group contained in the above product was separated by catalytical hydrogenation in isopropanol as a solvent in the presence of palladium, in using 12 grams of 1-phenyl-2-[N-benzyl-N-(1',1'-diphenyl-1'-hydroxy-propyl-(3))]-amino-3-propane as starting substance. When the reaction was finished, the filtrate was concentrated. Upon addition of dilute hydrochloric acid to the residue, there were obtained 7·5 grams of 1-phenyl-2-[1',1'-diphenyl-1'-hydroxy-propyl-(3')]-amino-propane-hydrochloride which was found to melt at 213-214°C.

Example 5

1-phenyl-2-[1'-meta-methoxy-phenyl-1'-phenyl-1'-hydroxy-propyl-(3')]-amino-propane.

According to the method described in Example 4, 35·7 Grams of ß-[N-benzyl-N-(1-phenyl-propyl-(2))]-amino-propiophenone, prepared from ß-chloro-propiophenone and N-benzyl-N-(1-phenyl-propyl-(2))-amine, were reacted with a Grignard solution, prepared from 8 grams of magnesium and 60 grams of meta-methoxy-bromobenzene in ether, and then worked up according to the method described in Example 4. The benzyl group was then separated in the manner described. 24 Grams of 1-phenyl-2-[1'-meta-methoxy-phenyl-1'-phenyl-1'-hydroxy-propyl-(3')]-amino-propane-hydrochloride were obtained, which was found to melt at 175-176°C.

Example 6

1-phenyl-2-[1',1'-diphenyl-1'-hydroxy-propyl-(3')]-amino-3-propane.

35·7 Grams of ß-[N-benzyl-N-(1-phenyl-propyl-(2))]-amino-propiophenone were reacted according to the method described in Example 4 with a lithium phenyl solution prepared with 4 grams of lithium and 40 grams of bromobenzene. Working up was effected in the manner described in Example 4. After separation of the benzyl group in accordance with the method described in Example 4, there were obtained 29 grams of 1-phenyl-2-[1',1'-diphenyl-1'-hydroxy-propyl-(3')]-amino-3-propane-hydrochloride, which was found to melt at 213-214°C.

Example 7

1-phenyl-2-[3'-phenyl-3'-hydroxy-pentyl-(1')]-amino-3-propane.

10 Grams of ß-phenyl-ß-hydroxy-N-(1-phenyl-propyl-(2))-N-benzyl-valeric acid amide were added to a suspension of 20 grams of lithium-aluminium-hydride in 500 ml of anhydrous ether, and the mixture was refluxed for 6 hours. The reaction mixture was decomposed with water and extracted with ether. The ethereal solution was then dried and the solvent was removed by destillation. There was obtained 3-phenyl-3-hydroxy-1-[N-1'-phenyl-propyl-(2')-N-benzyl-amino]-pentane. From this compound the benzyl group was separated in the manner described in Example 4. Upon addition of dilute hydrochloric acid to the filtered reaction mixture, there were obtained 2·4 grams of 1-phenyl-2-[3'-phenyl-3'-hydroxy-pentyl-(1')]-amino-3-propane-hydrochloride, which had a melting point of 161-163°C. The free base was found to melt at 93-95°C.

The ß-phenyl-ß-hydroxy-N-(1-phenyl-propyl-(2))-N-benzyl-valeric acid amide serving as starting material can be prepared, for example, in accordance with the method indicated in J. Am. Chem. Soc. 75, page 2415, from propiophenone and Li-[N-benzyl-N-(1-phenyl-propyl-(2))]-acetamide.

Example 8

1-phenyl-2-[1',1'-diphenyl-1'-hydroxy-propyl-(3')]-amino-propane.

11·1 Grams of 1,1-diphenyl-1-hydroxy-3-amino-propane and 3·9 grams of 1-phenyl-2-chloro-propane were heated for 3 hours on the oil bath to an internal temperature of 160°C. After having cooled, the reaction mixture was treated with dilute hydrochloric acid. There were obtained 5·8 grams of 1-phenyl-2-[1', 1'-diphenyl-1'-hydroxy-propyl-(3')]-amino-propane-hydrochloride which, after recrystallization from ethanol ester, was found to melt at 211-212°C.

Example 9

1-phenyl-2-[1',1'-diphenyl-propyl-(1')-ene-(3')]-amino-propane.

4·4 Grams of 1-phenyl-2-[1',1'-diphenyl-1'-hydroxy-propyl-(3')]-amino-propane were heated for about 15 minutes in 30 ml of toluene and 2 grams of para-toluene sulfonic acid until no more water separated off. After having cooled, the reaction mixture was rendered alkaline with 2N-sodium hydroxide solution and extracted with ether. The ethereal solution was dried and the solvent was removed by distillation. By addition of dilute hydrochloric acid the residue was converted into 1-phenyl-2-[1',1'-diphenyl-propyl-(1')-ene-(3')]-amino-propane-hydrochloride which after

recrystallization from ethanol/ether, was found to melt at 202-203°C. The yield was 2·5 grams.

We claim :

1. A process for the manufacture of basically substituted propanols of the formula shown in Fig. 1 of the accompanying drawings, in which R represents a hydrogen atom or the methoxy group, R_1 represents a phenyl radical that may be substituted by a methoxy group, or an alkyl group containing 1 to 4 carbon atoms, and R_2 represents a hydrogen atom or the methyl group, and of alkenyl amines obtainable therefrom by dehydration, which correspond to the formula shown in Fig. 2 of the drawings, in which R, R_1 and R_2 have the meanings given above, and of the acid addition salts thereof, which comprises :

(a) reacting a ß-[1-phenyl-propyl-(2)-amino]-propionic acid alkyl ester of the formula shown in Fig. 3 of the drawings, in which Y represents an alkyl group containing 1-5 carbon atoms and R_2' represents a hydrogen atom, a methyl group or a benzyl group, or a ß-[1-phenyl-propyl-(2)-amino]-ethyl-phenyl-ketone of the fromula shown in Fig. 4 of the drawings, in which R has the meaning given above and R_2' represents a hydrogen atom, a methyl group or a benzyl group, with organo-metallic compounds, and in case R_2' stands for benzyl, splitting off the benzyl group by means of activated hydrogen either during the reaction or following the preparation of the reaction products, or

(b) reducing phenylactone in the presence of basically substituted phenylpropanols by means of activated hydrogen, or reacting a basically substituted phenylpropanol with 1-phenyl-2-halogen-propanes, or

(c) reducing by means of activated hydrogen ß-hydroxy-ß-phenyl-carboxylic acid-N-[1-phenyl-propyl-(2)]-amides of the formula shown in Fig. 5 of the drawings, in which R and R_1 have the meanings given above and R_2 represents a hydrogen atom, to form the corresponding amines, and, if desired, dehydrating the saturated basic hydroxy compounds obtained by means of a dehydration agent into unsaturated compounds of the formula shown in Fig. 2 of the drawings, in which R and R_1 have the meanings given above and R_2 represents a hydrogen atom, and/or converting the compounds obtained into the corresponding salts by treatment with inorganic or organic acids.

2. Basically substituted propanols of the formula shown in Fig. 1 of the drawings, in which R represents a hydrogen atom or the methoxy group, R_1 represents a phenyl radical that may be substituted by a methoxy group, or an alkyl group containing from 1 to 4 carbon atoms, and R_2 represents a hydrogen atom or the methyl group, whenever prepared by a process as claimed in Claim 1 or an obvious chemical equivalent thereof.

3. Alkenylamines obtainable by dehydration of the products claimed in Claim 1 of the formula shown in Fig. 2 of the drawings, in which R, R_1 and R_2 have the meanings given in Claim 1, whenever prepared by a process as claimed in Claim 1 or an obvious chemical equivalent thereof.

4. Acid addition salts of the compounds claimed in Claims 2 and 3, whenever prepared by a process as claimed in Claim 1 or an obvious chemical equivalent thereof.

5. A pharmaceutical preparation suitable for oral or parenteral administration and having cardiac and circulatory properties, comprising as the active ingredient a compound as claimed in Claims 2 or 3 or a physiologically compatible acid addition salt thereof whenever prepared by a process as claimed in Claim 1 or an obvious chemical equivalent thereof, in admixture or conjunction with a pharmaceutically acceptable carrier and an auxiliary agent.

6. The 1-phenyl-2-[1',1'-diphenyl-1'-hydroxy-propyl-(3')]-amino propane, whenever prepared by a process as claimed in Claim 1 or an obvious chemical equivalent thereof.

7. The 1-phenyl-2-[1'-m-methoxy-phenyl-1'-phenyl-1'-hydroxy-propyl-(3')]-amino-propane, whenever prepared by a process as claimed in Claim 1 or an obvious chemical equivalent thereof.

8. The 1-phenyl-2-[3'-phenyl-3'-hydroxy-pentyl-(1')]-amino-propane, whenever prepared by a process as claimed in Claim 1 or an obvious chemical equivalent thereof.

9. The process for the manufacture of basically substituted propanols and of alkenylamines obtainable therefrom by dehydration conducted substantially as described in the Examples herein.

W. F. DEPENNING

FOR DEPENNING & DEPENNING,

Agent for the Applicants.

Dated this 23rd day of December 1960.

MGIP Santh.—IL—106 Patent/62—16·9·63—100.

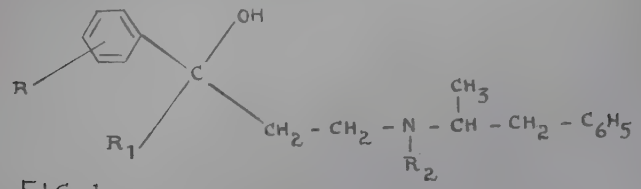


FIG. 1

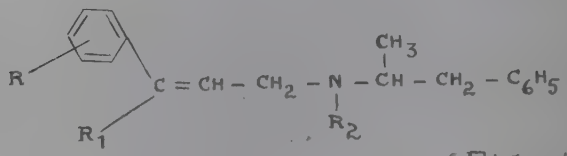


FIG. 2

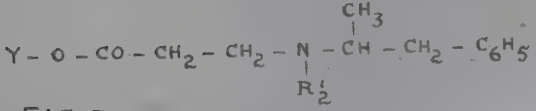


FIG. 3

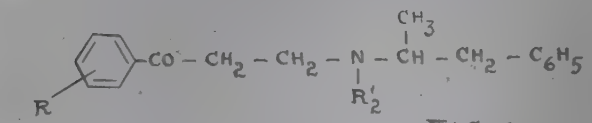


FIG. 4

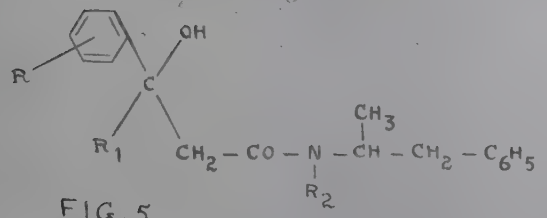
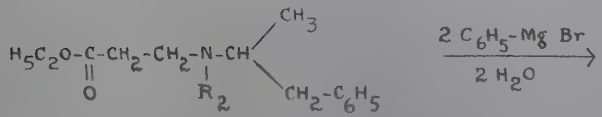


FIG. 5



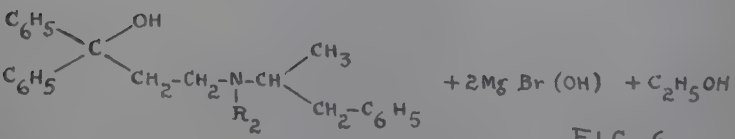


FIG. 6

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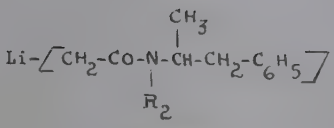

FIG. 7

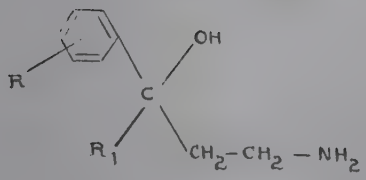

FIG. 8

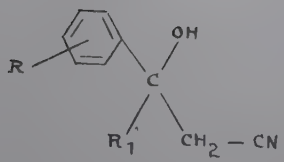

FIG. 9

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For INSPECTION CENTRE

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74658, filed 23rd December 1960, 2nd Paus 1882 (Saka.)
(Accepted 9th March 1962.)

LIFT SHAFT DOOR.

INVENTIO AKTIENGESELLSCHAFT, OF HERGISWIL, SWITZERLAND, A SWISS COMPANY.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

The present invention relates to a lift shaft door.

The door wings of lift shaft doors are mounted in known manner on hinges or on spindles, which have to take up the entire weight of the door. The use of relatively large hinges or spindles of correspondingly large dimensions is however often felt to be disturbing. According to the present invention a lift shaft door is proposed wherein no hinges are used. In accordance with the invention the door wing, mounted at top and bottom on spindles, is suspended in floating fashion for example by means of a torsion spring. The inner plate of the door which surrounds the torsion spring and the spindles is more expediently bent off about the axis of rotation of the door with a radius corresponding to the radius of rotation. Due to the proposed suspension of the door by means of a torsion spring the hinges are considerably relieved and can be made of substantially smaller dimensions.

An example of embodiment of the object of the invention is illustrated in the accompanying drawings wherein:

Figure 1 shows an elevation of the lift shaft door;

Figure 2 shows a horizontal section on a larger scale, along the line A—A in Figure 1;

Figure 3 shows a vertical section on a larger scale along the line B—B in Figure 2, and

Figure 4 shows a detail of the securing of the torsion spring.

As may be seen from Figure 1 of the drawings, the lift shaft door is constructed as single-wing door. The door wing 1 possesses an inner plate 2 and an outer plate 3, spindle mountings 4 and 5 respectively being secured by means of screws 6 to a cross-piece 2' at top and bottom respectively. Each spindle mounting 4 and 5 possesses a pertinent spindle 7 and 8, which spindles are guided in corresponding bushes, for example bearing bushes 9. The lower bush 9 is arranged in the threshold anglepiece 10 and the upper bush is arranged in the upper door transom 11.

The lower spindle mounting 4 is connected with the lower end of a torsion spring 12, which is secured at the other end at 13 to the door frame 13'. The end of the inner plate 2 is bent over with the radius r about the axis of rotation of the door, which radius corresponds to the radius of rotation of the door. Thus the object is achieved that even when the door is opened on the one hand the torsion spring and the spindle mountings remain invisible from the cabin side and on the other hand the end of the door wing does not project beyond the shaft edge. The more detailed construction of the spring securing may be seen from Figure 4. The upper end of the spring 12, which is formed as a leaf spring and initially tensioned, is received in a slot of a clamp screw 14 and held fast by a counter-sunk screw 15. The clamp screw 14 has an angular, for example hexagonal or octagonal, shank 16 and a round neck 17. The shank 16 is guided in a fixing plate 18, which possesses a hole corresponding to the shank cross-section and is connected by means of a bolt 19 with a mounting plate 20. The neck 17 of the clamp screw 14 is provided with a threading and carries a nut 21. The mounting plate 20 is secured in the door frame 13' for example by welding. In the described manner the entire door is suspended in floating fashion on the torsion spring 12, it being possible for a vertical adjustment of the door wing to be effected easily by means of the clamp screw 14 and the nut 21. Due to the rotation of the clamp screw 14 the initial tension of the spring 12 is varied. For this purpose the fixing plate 18 is lifted by means of the bolt 19, so that the arresting of the clamp screw 14 is released. The upper spindle 8 transmits the closing force to a door closure damping device, which can be arranged in the ordinary fashion. The spindle can further be used as connection for a concealed automatic door closer. The operating arm in this connection is on the one end secured to the spindle and co-operates at the other end with a slideway, so that the door is automatically opened and closed at the halting points.

We claim:

1. A lift shaft door, characterised in that the door wing mounted at top and bottom on spindles is suspended in floating fashion for example by means of a torsion spring.

2. A lift shaft door as claimed in Claim 1, characterised in that the inner plate of the door which surrounds the torsion spring and the spindles is bent off about the axis of rotation of the door with a radius corresponding to the radius of rotation.

3. A lift shaft door as claimed in Claims 1 and 2, characterised in that the torsion spring is connected on one end with the door wing and secured at the other end on the door frame.

4. A lift shaft door as claimed in Claims 1-3, characterised in that the spring is mounted for adjustment both vertically and also in the initial torsion force.

5. A lift shaft door as claimed in Claims 1-4, characterised in that one spindle is prolonged and is connected with a damper.

6. A lift shaft door as claimed in Claims 1-5, characterised in that one spindle is connected with the operating arm of an automatic drive arrangement, which operating arm co-operates at the other end with a slideway.

7. A lift shaft door, substantially as herein before described with reference to, and as shown in, the accompanying drawings.

B. DEPENNING

OF DEPENNING & DEPENNING,

Agent for the Applicants.

Dated this 23rd day of December 1960.

Price: TWO RUPEES.

MGIPC—L—19 Patent/62—29-9-62—100.

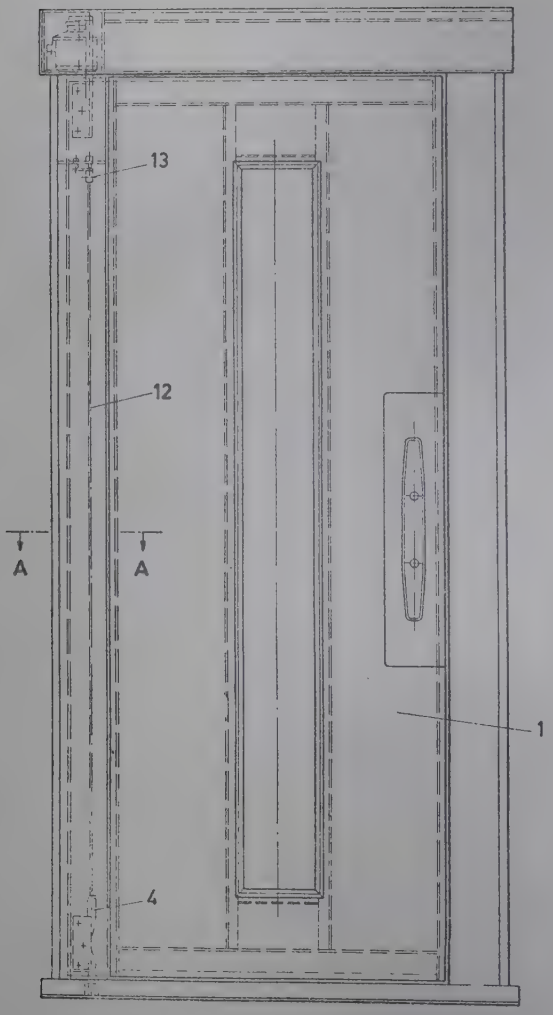

Fig. 1

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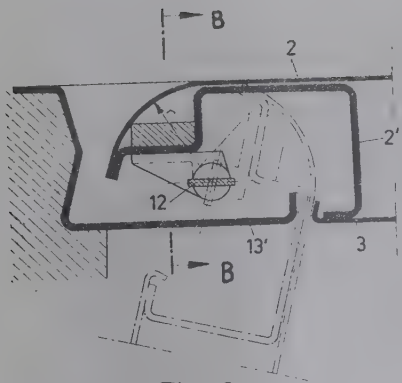

Fig. 2

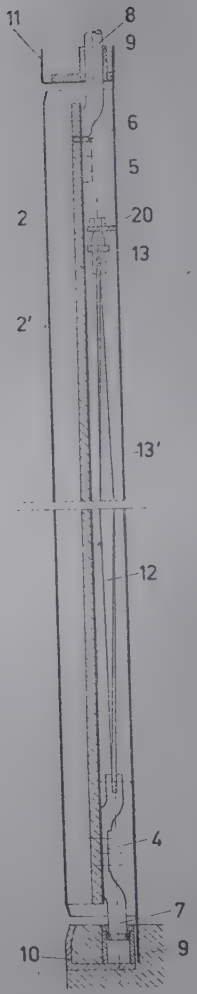

Fig. 3

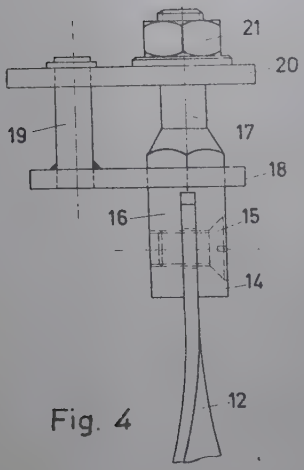

Fig. 4

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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74659, filed 23rd December 1960/2 Paus 1882 (Saka).

(Accepted 26th February 1962).

"IMPROVEMENTS IN OR RELATING TO ADJUSTABLE JOINTS FOR COLLAPSIBLE FRAMES OF CHAIRS, BEDS AND LIKE."

WILHELM BAHMULLER, OF PLUDERHAUSEN, WURTTEMBURGH, GERMAN FEDERAL REPUBLIC, A CITIZEN OF THE GERMAN FEDERAL REPUBLIC.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This invention relates to an adjustable joint for collapsible frames of folding chairs and beds, camping equipment, goods-display stands, racks and the like, which joint is provided with two pivot members capable of adjustment at various angles to each other and interconnected by a plate which is pivotally mounted at each end ; said joint is further provided with a loking element on one pivot member, which locking element co-operates in the various positions of use with a counter-member provided on the other pivot member in order to produce automatically the locking effect. In the case of known joints of this kind, for example, those employed on camp-beds with single-piece overlay, it occurs that when the user sits on the central portiion of the bed, thus causing a sudden tensioning of the overlay, the adjustable head-rest portion suddenly snaps upwards, frequently striking the head of the user. This is due to the fact that the known joints with automatically engageable and disengageable locking devices may be secured only against one direction of rotation. Locking devices which secure against both directions of rotation do not on the other hand operate automatically but must be engaged or disengaged by means of a hand lever. This factor is most unsatisfactory and inconvenient in the case of collapsible or folding equipment such as camp-bed, since it is not possible for the individual user to operate the locking device whilst at the same time adjusting or assembling the frame. It may also occur that the engaging of one of the locking has been overlooked, which may occasion accidents and damage to the other joints provided on the bed.

Moreover, in the case of known joints, the pivotally mounted ratchet is brought into the rest position by an automatic device employing a spring and is secured in this position until the head-rest portion is swivelled back into the initial position, so that such a device becomes ineffective when the spring fails to function, a not infrequent occurrence.

The object of the present invention is to obviate the above disadvantages by providing a simpler, more reliable and more comfortable structure which lends itself to mass-production.

According to the present invention, one pivot member is of double-arm construction, the short arm carying a locking element and a supporting surface, whilst the other pivot member is provided with a contact surface, for example of arcuate shape, whereby as the adjustable pivot member is swivelled upwards from the lowest to the highest position of use, the supporting surface strikes against the inner or outer face of the contact surface and then slides along it. The pressure produced by the lever affect produces a braking action to prevent the head-rest portion unexpectedly snapping upwards. This braking effect is also dependent upon the frictional, resistance occurring during swivelling of the connecting plate about the swivel point of the pivot member carrying the counter-piece. Furthermore, a ratchet is no longer necessary nor a pawl spring, because the locking element enters its counter-member by the lever action of the adjustable pivot member.

There is preferably provided on the connecting plate in the vicinity of the swivel point a locking edge which is sector-like, is of U-or L-shape, is flanged over, or is recessed and co-operates with at least one locking groove upon a further pivot member pivotally connected to the fixed pivot member and securable against rotation in either direction. The locking edge releases the latter pivot member only when the adjustable pivot member is folded over upon the fixed pivot member. Accordingly, when the user sists for example upon the central portion of the fixed pivot member of the bed, thus suddenly tensioning the one-piece overlay-the connecting plate, and consequently also the head-rest portion, is now held strongly in check.

In the case of the joint according to the invention, the automatic springless control means for preventing a locking action when the adjustable head-rest portion is returned to its lowest position of use, may be constructed in a most simple, reliable manner.

In addition, the shape of the joint is extremely compact. Even in a downwardly adjusted position of the head or foot-rest portion, the joint does not product any unevenness nor does it project noticeably beyond the surface of the chair or bed.

In the accompanying drawings, which illustrate two embodiments of the invention as applied to a camp-bed:

Fig. 1 shows an adjustble, lackable joint according to the invention, with the camp-bed in use, the back or leg-supporting portion being in the lowest adjusted position, shown in section at line passing through the axes of the pivot members and at right-angles to the pivotal axis ;

Fig. 2 shows the joint according to Fig. 1 in similar illustration, the pivot members being shown chain-dotted to indicate the folded position of the bed, and the full lines showing the position of the leg or lookable pivot member in use and the upper position of adjustment of the adjustable back or leg-supporting portion before it is pivoted downwards;

Fig. 3 shows the joint according to Fig. 1 in an unlocked intermediate position of the adjustable back or leg-supporting portion as it is swung downwards into its lowest position of adjustment in which the leg is looked, shown likewise in section on a line passing through the axes of the pivot membes;

Fig. 4 shows the joint according to Ftg. 3 in section on the line I-I of Fig. 3; and

Fig. 5 shows a further embodiment of a joint according to the invention in section cor-responding to the line I-I, Fig. 3.

Referring to tbo drawings :—

In all Figures the fixed joint arms, placed for example at the central portion of the camp bed are shown at 1, the members secured to the head-rest or leg-rest portion and which are adjustablo to various angular positions, are shown at 2, and members serving as legs which are securable against rotation in either direction, are shown at 3.

The lockable member 3 is pivotally connected by means of the bolt 4 to the fixed member 1. Also pivotally connected to said member 1 are the two connecting plates 6, pivoting at the rivet 5, said plates being further pivotally connected at their other extremity to the adjustable pivot member 2 upon the bolt 7. The rivet 5 also serves asswivel pin for the control lever 8 which is rotatable between the plates 6 which are here curved fork-like. Also rigidly secured to the bolts 4 and 5 are the toothed locking discs 10 located between the two lateral walls 9 of the pivot member 1 and on both sides of the plates 6 or as the case may be, of the pivot member 3. In the embodiment according to Fig. 5 these are not employed.

The short lever arm 11 of the member 2 carries toothed or wedge-shaped locking elements 12 and bearing surfaces 13, as shown in Figs. 4 and 5. Correspondingly, the edges of the lateral walls 9 of the member 1 are inwardly flanged as far as their upper terminal edges 15 (see Figs. 1 and 2) to provide arcutact contact surfaces 14. The supporting surfaces 13, on the other hand, co-operate with the checking lug 16 of the control lever 8, which lug may also strike against the upper stop 17 on the locking disc 10 (Fig. 2) whilst the lower stop 18 of the locking disc 10 can also check the lug 19 also provided on the control lever 8.

Within the area of the plates 6 the lockable pivot member 3 is provided with two arcuate, inwardly directed locking flanges 20 which, in the position of use of the pivot member 3, engage in the sector-like locking edges 21 which are beat off to U-shape at a suitable area of the plates 6. At the point between U-shaped and circular cross-sections of the adjustable member 2, a limiting stop member 22 is provided which co-oparates with the plates 6 and determines the extent of pivot of the member 2 about the bolt 7. The extremity of the short lever arm 11 is also rounded off or tapered off or towards the centre of the plates so that, when the pivot member 2 is brought back, the point 23 on the arm 11 remotest from the point of rotation at the bolt 7 comes firstly into contact with the outer edge 15 of the supporting surfaces 13.

The manner of woking of the new joint is as follows:

From the position shown chain-dotted in Fig. 2, with the pivot members 2 and 3 lying parallel (camp-bed in folded position) firstly, the pivot member 3 acting as the leg of the chair is swung out in the direction shown by the arrow into the position of use which is shown in full lines and extends slightly beyond the vertical. The adjustable back for leg-rest portion with the pivot member 2 is then rotated in the direction shown by the arrow (anti clockwise). Thus, the member 2 rotates firstly about the bolt 7 into the position shown in full lines, until its supporting surface 13 strikes against the lug 16 of the control lever 8 which in its upper position lies against the stop 17. Meanwhile, the point 23 at the end of the lever arm 11 slides past the outer edge 15 and the locking member 12 enters the area between the lateral walls 9 but not to such an extent that it engages with the teeth of the locking disc 10. Since the pivot point at the bolt 7 is now ineffective, as downward rotation proceeds (Fig. 3) the control lever 8 with the plate 6 follows the rotation about the pivot point at the bolt 5. Shortly before the lowest position of use is reached the lug 19 of the control lever 8 strikes against the lower stop 18 so that it ceases to accompany the rotation; the supporting sufaces 13 slide past the lug 16 and are finally released, whereupon the locking member 12 now engages the teeth of the locking disc 10 and then occupies its bottom working position, as shown in Fig. 1. At the same time, locking edges 21 of the plate 6, as they rotate about the point 5, engage the locking grooves 20 of the pivot member 3, thus securing said member automatically against rotation in either direction.

The adjustable pivot member 2 (for example, of the head-rest portion of the camp-bed) can now be rotated upwards (see arrow, Fig. 1) from this bottom position of use, into various angular positions of engagement with the teeth of the locking disc. In this case, the pivot member 2 rotates firstly about the bolt 7 until its supporting surfaces 13 strike against the contact surface 14 (Fig. 4) and then slide along this, at which point the pivot point at the bolt 7 becomes ineffective so that the plates 6 are both rotated with the control lever 8 about the bolt 5. When the desired angular position is reached, the locking element 12 engages the locking disc 10 by exerting a slight downward pressure, i.e. easing of the member 2.

When a person sits on the central portion of the bed associated with the fixed member 1, thus sharply tensioning the single-piece fabric overlay, the tendency is for the tension thus produced to pivot the adjustable member 2 upwards (clockwise in Fig. 1). The first stretching or tensioning effect upon the overlay is then absorbed by a slight pivoting of the member 2 about the bolt 7 out of the particular working position of the locking element 12 until the supporting surfaces 13 strike against the contact surfaces 14. At the same time, due to the leverage occasioned by the sudden, heavy stress applied to the central portion and its pivot member 1, as also to the pivot member 3 now in its fully extended position of use, the locking grooves 20 of said member 3 are pressed against edges 21 of the plates 6 so that these latter are clamped in position. This clamping action, assisted by friction at the bolt 5 about which alone the pivot member 3 can now rotate, produces an increase in pressure between the supporting surfaces 13 and contact surfaces 14, whereby the remaining stretch action of the overlay is practically nullified, or is at least so throughly held in check that the back portion on the pivot member 2 cannot strike against the head of the user.

As the adjustable member 2 is further swivelled through the top working position, the lug 26 of the control lever 8 which until now has followed the rotation, is checked by the upper stop member 17, whereupon the supporting surfces 13 come to rest upon the lug 16. From this position, the adjustable member 2 may now be swivelled back (Fig. 3) into the bottom position of use as shown in Fig. 1. If, on the other hand the bed is folded completely, i.e. the pivot member 2 is further rotated into the chain-dotted position of Fig. 2, the supporting surfaces 13 with the point 23 on the lever arm 11 leave the contact surfaces 14 at their outer edge 15 whereupon the pivot point at the bolt becomes ineffective; the pivot member 2 now continues to rotate upon the bolt 7 until its limiting stop 22 comes into contact with the plates 6 which follow the rotation until the end position is reached; meanwhile, the member 3 is also released.

This arrangement of the outer edge 15, the point 23 and the limiting stop 22 ensure that, as the pivot member 2 is swivelled in the directions indicated by the arrows in Fig. 2, the supporting surfaces 13, or as the case may be the locking element 12 enter firstly into the area between the lateral walls 9, and then slide along the *inner* faces of the contact surfaces 14, or as the case may be, strike against the lug 16. These control means with the stop 17 and the edge 24 on the short lever arm 11 may also be so construoted that they cause the plates 6 to rotate a few degrees in the opposite direction of rotation after the supporting surfaces 13 have left the contact surfaces 14 and the outer edge 15. As the pivot member 2 is then swuelled downwards, as in Fig. 3, the supporting surfaces 13, or locking element 12 slide along the *outer* face of the contact surfaces 14 and pass through recesses in the surfaces 14 in the vicinity of the lower stop 18, once again into the bottom position of use, as in Fig. 1. In this case the control lever 8 is no longer required, since the contact surfaces 14 prevent the occurrance of the locking action. Morever, the supporting surfaces

13 may be fitted to the edge 24 of the short lever arm 11 so that, as the pivot member 2 is swivelled upwards, these surfaces slide along the outer faces of the contact surfaces 14, thus producing the braking effect.

In the case of the embodiment of the joint as shown in Fig. 5, instead of the locking discs 10 which are here dispensed with, the lateral walls 9 of the fixed pivot member 1 are preferably constructed as conical locking cups 10, and the locking element 12 is of wedge-shape so that in any desired working position (as distinct from tooth positions) the latter is wedged to the locking cups under the lever action of the pivot member 2. In the case of this arrangement, the method of control may remain as already described above. It is evident that the locking discs 10 or locking element 12 may also be fork-shaped or wedge-shaped, that is to say conical.

In the embodiments described the control lever is mounted on the bolt 5 between the plates 6. During upward pivoting, in order to render the point of rotation at the bolt 7 ineffective, in other words to prevent the locking action, a control lever or slide may be rotably mounted on the short lever arm 11 or on the plates 6 so that it is supported against the plate 6 or lever arm 11 and is brought into and out of operation by suitable stops 17 and 18 on the fixed pivot member 1.

As will be observed from Fig. 4, the lockable pivot member 3 provided with two identical locking grooves 20. It is therefore also possible, by means of the bolt 5, to have two lockable pivot members 3, each with only one identical locking groove 20, pivotally mounted so that these may be swivelled separately or both together and may be locked against rotation in either direction. A further possibility is to employ two separately adjustable pivot members 2 of identical construction which are pivotally connected each separately to at least one identical connecting plate
6. The other ends of the plates 6 are pivotally secured by the bolt 5 to the fixed pivot member 1, and the pivot members 2 co-operate with identically arranged control means 8 or 14 and stop members 17 and 18. This embodiment is advantageously employed for collapsible frames of display, stands, sports equipment, tent-poles and the like.

Finally, the pivot member 2 of double-arm construction may also be employed as a fixed pivot member.

The joint according to the invention may be produced from steel, or plastics, or jointly from these two materials. Where plastics material is employed, steel inserts may be embedded therein.

I CLAIM :—

1. A joint for collapsible frames of chairs and beds, camping equipment, sports equipment, goods-display stands, racks and the like, which is provided with two pivot members capable of adjustment at various angles to each other and interconnected by a plate which is pivotally mounted at each end, said joint being further provided with a locking element on one pivot member, which locking element co-operates in the various positions of use with a counter-member provided on the other pivot member in order to produce automatically the locking effect; said joint having one pivot member of double-arm construction, the short arm carrying a locking element and a supporting surface whilst the other pivot member 1 is provided with a contact surface, for example of arcuate shape, whereby, as the adjustable pivot member is swivelled upwards from the lowest to the highest position of use, the supporting surface strikes against the inner or outer face of the contact surface and then slides along it.

2. A joint according to claim 1, wherein the locking element is in the form of a ratchet-like organ with a projection bearing tooth-formations, whilst its counter member is a correspondingly toothed locking disc, rigidly mounted for example on a swivel point, said locking element producing in its various positions of use the the locking effect under the lever action of the adjustable pivot member.

3. A joint according to claim 1, wherein the locking element or counter-member is wedge-shaped or fork-like that is to say conical so that, in the various working positions, due to the lever action of the adjustable pivot member, these are wedged against corresponding counter-surface of the counter member or locking element respectively.

4. A joint according to claim 3 wherein the lateral walls of the pivot member for example the fixed pivot member, are constructed as counter-member in the form of conical locking cups, with the inner or outer faces of which the locking element, provided with wedge-shaped or fork-like surfaces, co-operate.

5. A joint according to claim 1 wherein the edges of the lateral walls of the pivot member, for example the fixed pivot member, are curved, preferably inwardly to form arcuate contact surfaces and also possess, in the region before the bottom and after the top working positions of the adjustable pivot member, suitable recesses or stop members co-operating with similarly formed supporting surfaces or with the locking element in such a manner that, as the adjustable pivot member is swivelled from its top to its bottom position of use, these contact the outer faces of the contact surfaces and slide along said surfaces, whereby engagement of the locking element at this point also under the lever action, with its counter member cannot occur and consequently the check action is automatically prevented.

6. A joint according to claim 1, characterised in that at least one control lever or slide is rotatably or slidably mounted at a bolt on the plate or on the short lever arm of the double-arm pivot member, which control member is automatically brought into and out of operation by suitable stops whereby, as the adjustable pivot member is swivelled downwards, the locking element is prevented from engaging with its counter-member.

7. A joint according to claim 6, in which the locking lever is rotatable about the swivel point, and the control lever has a supporting arm and a contact arm and is preferably so constructed and so mounted on the common swivel point between the forked portions of one plate at one of the swivel points or between two suitable formed plates that it is caused by friction to follow the rotation of the plate or plates throughout the range of adjusted positions of the adjustable pivot member and it co-operates automatically with the stops and the supporting surface in such a manner that it prevents a locking action only when the adjustable pivot member is swivelled from its top to its bottom position of use.

8. A joint according to any preceding claim, wherein the extremity of the lever arm, preferably of U—shaped cross-section, that is to say, of the locking element or supporting surface 13, is rounded off or tapered off in the direction of the centre of the plate, so that the point of the edge thus formed and which is remotest from the swivel point of the adjustable pivot member slides past the upper terminal edge of the contact surface when the short lever arm is swivelled inwards between the two lateral walls of the fixed pjivot member.

9. As joint according to any preceding claim, wherein a miting stop member co-operating with the plate is so mounted on the adjustable pivot member that rotational of the adjustable pivot member about the swivel point is prevented shortly before side pivot member reaches the final folded position, whereby the plate is further swivelled about the point.

10. A joint according to any preceding claim, wherein a locking edge formed on the plate in the region of the

swivel point, and which is sector-like, for example of U-or L-shape, is flanged over or is recessed, co-operates with at least one locking groove of a further pivot member pivotally connected to the fixed member and securable against rotation in either direction, which locking edge releases the pivot member only when the adjustable member is folded over against the fixed member.

11. A joint according to claim 10, wherein the locking groove and locking edge are so constructed that, due to the lever action of the lockable pivot member in its outwardly extended position of use, when there is a certain increase of load on the portion located on the fixed pivot member, these organs produce a braking effect on the rotation of the plate and consequently also upon the sudden, undesirable upward swivelling of the adjustable pivot member.

12. A joint according to claim 10, wherein two pivot members provided with identical locking grooves are pivotally mounted on the swivel point, whereby said pivot members may be swivelled, either separately or both together, into their rest position or position of use and may be thus secured against rotation in either direction.

13. A joint according to any preceding claim, wherein two identically formed, separately adjustable pivot members are each pivotally connected to at least one identical plate, the other extremities of said plates being rotatably secured to acommon swivel point on the fixed pivot member, and the pivot members co-operating with identically arranged control means and stop members.

14. Joints substantially as hereinbefore described with reference to the various Figures of the accompanying drainge.

G. S. DAVAR
of L. S. DAVAR & CO.,
Applicant's Attorneys.

Dated this 23rd day of December 1960.

Printed by The Nelys Printing Works, Calcutta-1.

NO. 74659 OF 1960.

NAME : WILHELM BAHMULLER.

TWO SHEETS.

SHEET .. ONE.

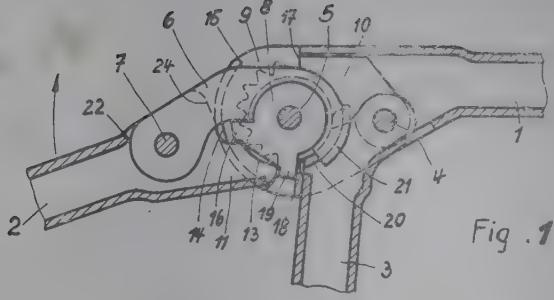


Fig. 1

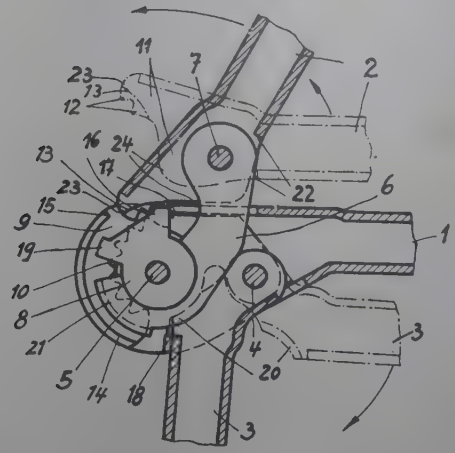


Fig. 2

L. S. DAVAR
OF L. S. DAVAR & CO.
APPLICANT'S ATTORNEYS.

NO. 74659 OF 1960.

NAME : WILHELM BAHMULLER

TWO SHEETS.

SHEET .. TWO.

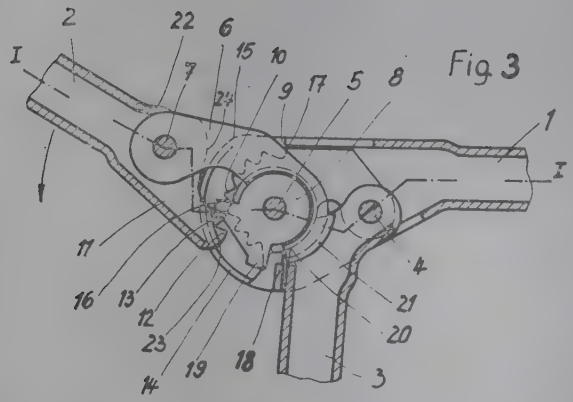


Fig. 3

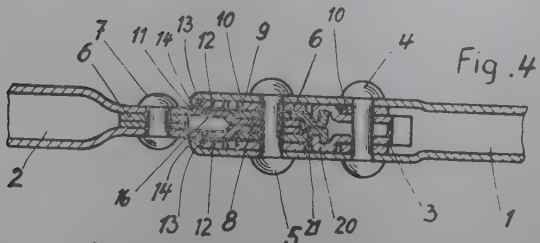


Fig. 4

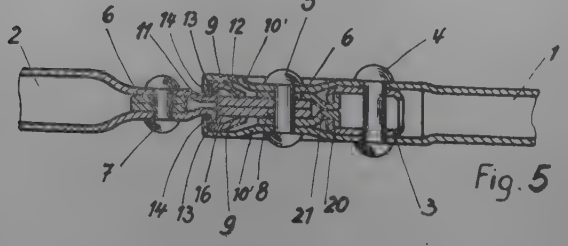


Fig. 5

L. S. DAVAR
OF L. S. DAVAR & CO.
APPLICANT'S ATTORNEYS.

FOR INSPETCION CENTRE

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74662, filed 24th December 1960/3 Paus. 1882 (Saka)

(Accepted 6th June 1962.)

"IMPROVED CIGARETTE CASE."

BULCHAND TIKAMDAS KRIPALANI, A HINDU, INDIAN SUBJECT, BEING THE SOLE PROPRIETOR CARRYING ON BUSINESS UNDER THE NAME AND STYLE OF PARAMOUNT PLASTIC, OF 6, FREE SCHOOL STREET, CALCUTTA-16, WEST BENGAL, INDIA.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This invention relates to improved type of cigarette cases.

For the convenience of smokers, various types of cigarette cases of various designs and constructions have been proposed in the art. In several hitherto known devices, the case usually consists of a space for 10 or 20 cigarettes. With the withdrawal of each cigarette, a space is created in the case, the cigarettes are shaken loose, the ends of the cigarettes get damaged owing to friction with each other and dust is likely to form from the flake. Moreover due to creation of air space in the case, the aroma of the remaining cigarettes is lost, and the cigarettes become stale.

The principal object of this invention is to enable the cigarettes to be drawn out of the case one by one, without disturbing the sequence and arrangement of the remaining cigarettes in the case. Thus the cigarettes do not shake loose during the time the case is carried in the smoker's pocket and dust formation does not take place and the cigarettes will ever remain fresh due to non-formation of air space in the case.

Thus with the above objects in view, this invention provides an improved cigarette case which consists of a plurality of individual chambers arranged side by side, each said chamber being shaped and adapted to enclose a cigarette and is characterised in that said chambers are formed by a plurality of I-shaped partition pieces disposed side by side and held together by springs. In a particularised embodiment, the said I-shaped partition pieces are held together by means of two lengths of helical springs passing through holes or slots provided at the top and the bottom portions of the partition pieces.

The I-shaped partition pieces are made of plastic material e.g., of polythene, polystyrene, urea-formaldehyde resin, melanine-formaldehyde resin, methyl methacrylate resin, bakelite and the like.

In order that the invention can be fully understood, it will now be described with the help of the accompanying drawings in which—

Fig. 1 represents perspective view of the cigarette case ;

Fig. 2 is an exploded view of the cigarette case ;

Fig. 3 represents sectional view on line A-B of Fig. 1.

Referring to the figures of the drawings, the cigarette case is composed of a plurality of I-shaped partition pieces 1 disposed one after another so that each two adjacent pieces together form a chamber 5 for storing a cigarette therein. Each of the partition pieces 1 is provided at its top and bottom thereof with holes or slots 2 wherein the axis of the holes is at right angle to the longitudinal axis of the partition piece 1. The series of the slots 2 at the top are co-axial with each other so as to form a continuous passage for a strand of helical spring 3 to pass through. Similarly a second strand of helical spring 4 passes through the slots 2 at the bottom of the cigarette case. In the normal position in the springs 3 and 4 tend to hold the partition pieces 1 closely to form a series of closed chambers 5 so that the cigarettes placed in these chambers 5 will not fall out. The springs 3 and 4 are held by studs 6 screwed on to the ends of the springs as shown at 6 in the figs 1 and 2, Each chamber 5 is so shaped as to encase single cigarette therein.

For withdrawing, the smoker will bend the case in a direction transverse to the axis A-B of Figure 1 and take out the cigarette from any chamber.

What has been disclosed herein are illustrative and any changes or modifications thereof are possible without departing from the spirit and scope of the invention as defined by the appended claims.

I Claim :—

1. An improved cigarette case consisting of a plurality of individual chambers arranged side by side, each said chamber being shaped and adapted to enclose a cigarette and is characterised in that said chambers are formed by a plurality of I-shaped partition pieces disposed side by side inside the case and held together by springs.

2. A cigarette case as claimed in Claim 1 wherein the top and bottom portions of said each partition piece is provided with a hole or slot through which pass two helical springs to hold the partition pieces securedly in assembled condition.

3. A cigarette case as claimed in above claims wherein said partition pieces are made of plastic materials.

4. An improved cigarette case substantially as herein described and illustrated in the accompanying drawings.

(A. Saha)
of Trade Mark Registration Bureau
Applicant's Attorney.

Dated this 24th day of December 1960.

Price : TWO RUPEES.

Printed by The Nelys Printing Works, Calcutta-1.

NO. 74662 OF 1960

One Sheet.

B.T. Kripalani

FIG. 1.

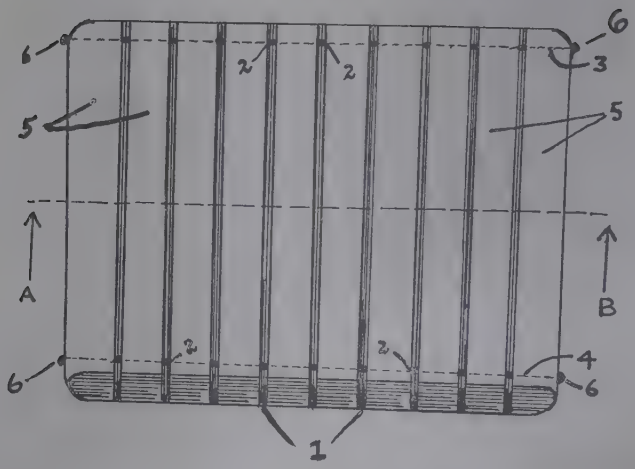


FIG. 2.

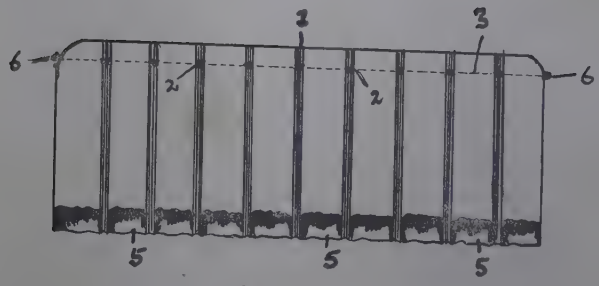
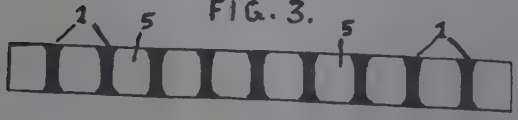


FIG. 3.



Ambale

OF Trade Mark Regn. Bureau

Applicants, Attorney.

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74663. Application No. 74663, dated 24th December 1960. Complete Specification left on 23rd February 1961. (Application accepted 3rd September 1962.)

IMPROVED DREDGER.

PROVISIONAL SPECIFICATION

MENACHERRY ITTIKURIYA PAUL, Ex-M.L.A., Narakal, Kerala State, subject of the Indian Union and Mampilly George Kurien, Mariden, 371, Nagawadi, Bandra, Bombay 50, subject of the Indian Union.

The following specification describes the nature of this invention.

Vast shallow places in back waters near coastal areas are now left undeveloped having no proper bunding and reclamation needed for agricultural operations (mainly paddy cultivation) due to the non-availability of mud and sand at less cost to protect them against monsoon floods. To remedy this situation this invention of the pattern—the model dredger with buckets on both sides of the body designed to excavate mud and sand from river bottom easily and which is not in use in India by any other person will very economically serve the above desired purposes of such wet lands to be easily converted into pucca cultivable fields and to be within the means of poor middle class cultivators to promote food production, both intensive and extensive.

In the accompanying drawings a dredger according to our invention is shown.

Illegible

Dated this 22nd day of December 1960.

COMPLETE SPECIFICATION.

MENACHERRY ITTIKURIYA PAUL, Ex-M.L.A., Narakal, Kerala State, subject of the Indian Union and Mampilly George Kurien, Mariden, 371, Nagawadi, Bandra, Bombay 50, subject of the Indian Union.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

The invention pertains to an improved dredger capable of excavating mud or clay at double the rate at which it is done by the conventional one. The dredger in question has two separate bucket conveyor lines which scoop material simultaneously and delivers to barges or boats standing by it.

This dredger is ideally suited for excavation of mud or clay from canals, rivers or back-water areas. The excavated material may be conveniently loaded into country boats or barges for subsequent utilisation for reclamation of coastal areas or for construction of bunds in shallow cultivating fields.

An embodiment of our invention is described herein below with reference to the accompanying drawings, in which :

Fig. 1 represents the side view of the Dredger.

Fig. 2 represents the aerial view of the Dredger.

Fig. 3 represents the ratchet set up in the winch and ratchet mechanism.

At one end of the boat or floating body 10, two stand beams 6 are fixed, one at each side of the boat or floating body, such that their upper ends project outwardly of the boat or floating body. A high level shaft 4 is rotatably supported at the top of the beams 6 with the help of bearings 20. A low level shaft 5 of length equal to the shaft 4 is arranged at the other end of the boat or floating body 10 in a hanging position on a rope 12, passing over the pulley 13 with its one end connected to the centre of the shaft 5 and the other end to the winch set 14 so that it can be raised or lowered by the ratchet (Fig. 3) with the help of the winch set 14 so fitted for the purpose. Like the shaft 4 the ends of the shaft 5 project outwardly of the boat of floating body at the opposite sides of the same. At each end of the two shafts 4 and 5 a sprocket wheel 3 is fixed at the ends of the shafts 4 and 5, it being non-rotatable in relation to the shaft 4, but is rotatable in relation to the shaft 5. On one side of the boat or floating body 10, over the sprocket wheels 3 at the ends of shafts 4 and 5, an endless link belt chain 2 fitted with buckets 1 is arranged to run. Similarly on the other side of the boat or floating body another link belt chain runs over the other sprocket wheels at the ends of the shafts 4 and 5. The channel beams 11 connect their ends with the shafts 4 and 5 at each side of the boat or floating body 10, both the shafts being rotatably fitted in relation to the channel beams 11. The channel beams 11 and the two shafts 4 and 5 together make a rectangle. The buckets 1 are fixed on the outer side of the link belt chain 2 so that they avoid the sprocket wheels 3, when the belt chain 2 runs over the sprocket wheels 3. A driving chain 7 is made to pass over the two sprocket pulleys 15, one fixed to the high level shaft 4 at its centre and the other belonging to the reduction gear and clutch mechanism 8 connected to the engine 9 by another chain 16 passing over two sprocket pulleys 17 of which one is fixed to the shaft 18 of the reduction gear and clutch mechanism and the other fixed to the shaft 19 of the engine 9. On operation, when power is transmitted to the driving chain 7 by the engine 9, the high level shaft 4 rotates with the sprocket wheels 3 and automatically the link belt chain 2 with the buckets 1 move from the high level shaft 4 to the low level shaft 5 and *vice versa* in a cycle order. The buckets 1 are so arranged that when they move without load from the high level shaft 4 to the low level shaft 5 they are in the inverted position and when they move with the load viz. the mud scooped by the same from the low level shaft to the high level shaft they are in the upright position. By raising or lowering the low level shaft 5 sufficiently for the buckets 1 to come in contact with the mud beds or clay under the water, each bucket 1 is enable to excavate the mud or clay from such depth of water as the low level shaft 5 is allowed to go into. Due to the forward motion of the floating body 10 to the direction of the low level shaft 5, the material scooped is carried by buckets 1 to the high level shaft 4 in the upright position and after each bucket 1 comes at the top of the sprocket wheels 3 of the high level shaft 4, the bucket 1 automatically gets inverted and the materials are dumped to the waiting boats standing by at the rear of the floating body 10.

We claim :

1. An improved dredger comprising of a boat or floating body, two link belt chains fitted with buckets, provided one on each side of the boat or floating body, one belt chain passing over a pair of sprocket wheels arranged at the ends of a high level shaft and a low level shaft at one side of the boat or floating body and the other passing over another pair of sprocket wheels arranged at the other ends of the said shafts on the other side of the boat or floating body, one of the said shafts being arranged at the front of the boat or floating body and the other at the rear of the same and the said shafts being so arranged that opposite ends of each said shaft project outwardly of the boat or floating body at the opposite sides of the same, the high level shaft being rotatably supported on stand beams fixed on the boat or floating body and the low level shaft being suspended on a rope connected to a winch and ratchet mechanism so that it can be raised or lowered by the same, the sprocket wheels on the high level shaft being fixd to the same and the sprocket wheels on the low level shaft being rotatable in relation thereto, a pair of channel beams provided one at each side of the boat or floating body and connecting the said two shafts at the ends, such that both the shafts being rotatable in relation to the channel beams, and an engine coupled to the high level shaft with the help of engine drive means through a reduction gear and clutch mechanism.

2. An improved dredger as claimed in Claim 1 and substantially as described with reference to the accompanying drawings.

Illegible

Dated this the 20th day of February 1961.

MGIP Santh.- SL—151 Patent/62—21-10-63—100.

Price : TWO RUPEES.

PROVISIONAL

1. MENACHERRY ITTIKURIYA PAUL.
2. MAMPILLY GEORGE KURIEN.

NO. 74663.

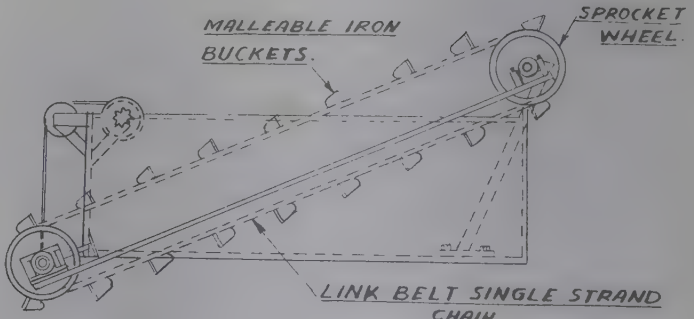


FIG. No. 1.

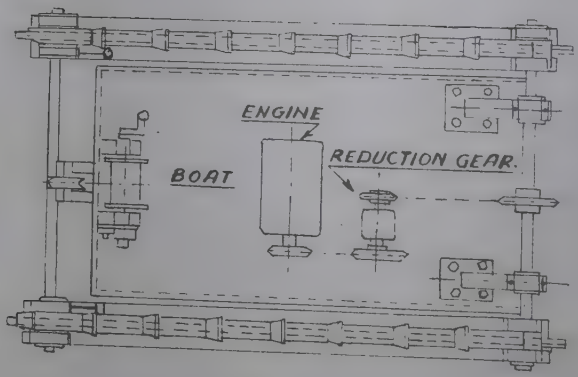


FIG. No. 2.

FIG. No. 3.

1. [signature]
2. [signature]

REG. NO. 2273 E/44—106'64.

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COMPLETE

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1. MENACHERRY ITTIKURIYA PAUL
2. MAMPILLY GEORGE KURIEN

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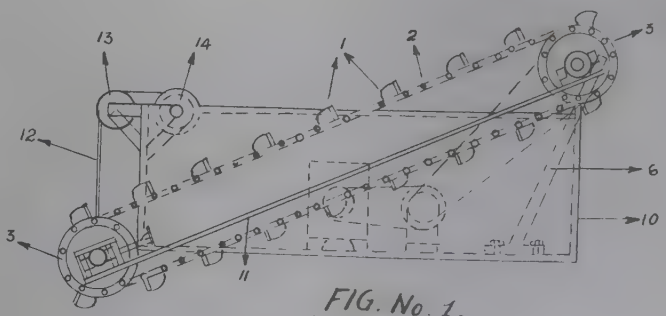

FIG. No. 1.

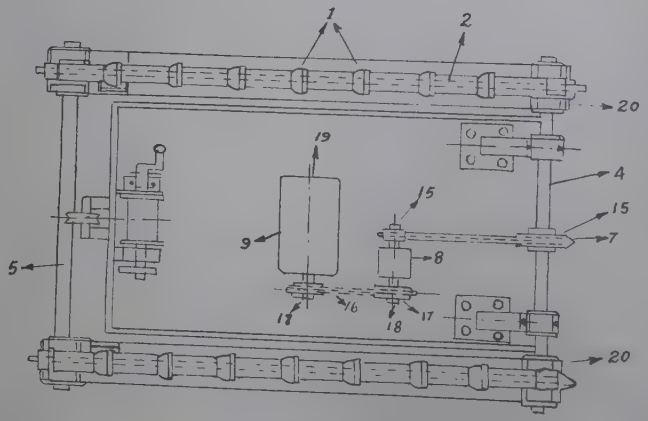

FIG. No. 2.

FIG. No 3.

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2. [illegible]

REG. NO. 2273 E/44—106'54.

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NUMBER OF SHEETS 1.
SHEET No. 1.

1. MENACHERRY ITTIKURIYA PAUL
2. MAMPILLY GEORGE KURIEN

NO. 74663.

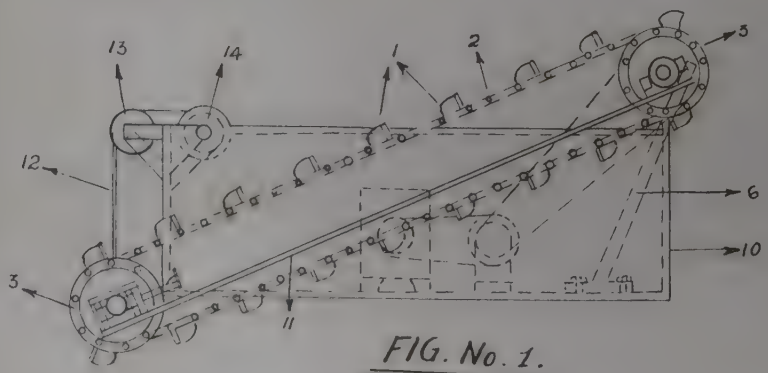

FIG. No. 1.

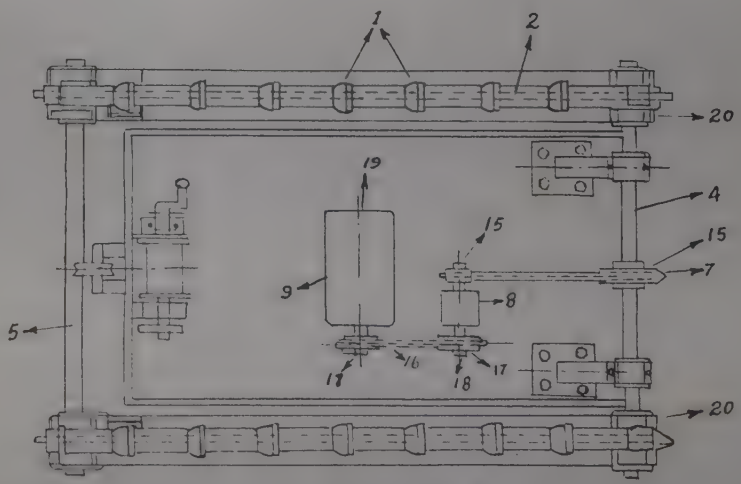

FIG. No. 2.

FIG. No 3.

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2. [illegible]

REG. NO. 2273 E/44—106'64.

PRINTED AT THE SURVEY OF INDIA OFFICES, (P. L. O.).

restraining the locking jaws mentioned in their locked position.

A further object of the invention is to provide a railway car for transporting a road semi-trailer of the type including a rear end carrying road wheels of standard road gauge; wherein the railway car comprises a longitudinally extending narrow centre sill, a pair of longitudinally extending and laterally spaced-apart stationary platforms respectively carried on the opposite sides of the centre sill and projecting laterally outwardly therefrom and disposed below the top thereof and constituting a roadway of standard road gauge, the roadway being arranged to engage and to support the road wheels of the semi-trailer so as to mount the same upon the top of the centre sill in straddling relation therewith in order to accommodate movements of the mounted semi-trailer longitudinally along the centre sill, and further comprising a pair of longitudinally extending and laterally spaced-apart wheel guides respectively carried by the opposite sides of the centre sill and each disposed outwardly of the adjacent side thereof and below the top thereof and above the associated one of the platforms and adjacent to the inner edge thereof, wherein each one of the wheel guides is adapted to engage the inside surface of one of the road wheels carried by a semi-trailer mounted upon the top of the centre sill incident to longitudinal movement of the semi-trailer along the centre sill in the event of substantial misalignment between the centreline of the centre sill and the centreline of the semi-trailer, whereby the one wheel guide exerts a reactive force laterally outwardly upon the engaged inside surface of the one road wheel tending to rotate the rear end of the mounted semi-trailer in order to minimize the misalignment mentioned thus to effect centering of the mounted semi-trailer with respect to the centre sill.

A still further object of the invention is to provide an improved railway car for transporting indiscriminately road semi-trailers of first and second types, wherein the first type of semi-trailer includes a rear end carrying road wheels of standard road gauge and the second type of semi-trailer includes a rear end carrying both road wheels of standard road gauge and track rollers of given narrow gauge depending therefrom and disposed inwardly of and above the road wheels carried thereby; and wherein the railway car comprises a longitudinally extending narrow centre sill, a pair of longitudinally extending and laterally spaced-apart stationary rails respectively provided on the opposite top sides of the centre sill and constituting a trackway of the given narrow gauge, and a pair of longitudinally extending and laterally spaced apart stationary platforms respectively carried on the opposite sides of the centre sill and projecting laterally outwardly therefrom and disposed below the top thereof and constituting a roadway of standard road gauge, the roadway being arranged to engage and to support the road wheels of the first type semi-trailer so as to mount the same upon the top of the centre sill in straddling relation with the trackway and with the underportion thereof positioned above the trackway and out of contact therewith in order to accommodate movements of the mounted first type semi-trailer longitudinally along the centre sill, the trackway being arranged to engage and to support the track rollers carried by the second type semi-trailer so as to mount the same upon the top of the centre sill with the road wheels thereof projecting laterally outwardly over the roadway and with the road wheels thereof positioned above the roadway and out of contact therewith in order to accommodate movements of the mounted second type semi-trailer longitudinally along the centre sill.

Accordingly the present invention provides a hitch for a road semi-trailer comprising a pair of longitudinally extending and laterally spaced-apart supports, an element extending laterally between said supports and mounted at the opposite ends thereof upon said supports for rotation about a given axis, a standard rigidly secured at the lower end thereof to the intermediate portion of said element whereby said standard is mounted for pivotal movement with said element and about the axis thereof extending transversely of said supports, said standard being selectively pivotally movable between a storage position and an erected position, said standard in its storage position being disposed between said supports and in its erected position being disposed from between said supports, a motion limiting and cushioning device carried by said supports, latching mechanism having a set position connecting said standard to said device and a trip position disconnecting said standard from said device means responsive to pivotal movement of said standard into its erected position for setting said latching mechanism, said standard in its erected position being biased by said connected device into a normal upstanding attitude and being pivotable fore-and-aft with respect thereto longitudinally of said supports against the bias of said connected device, means operative to trip said latching mechanism, said standard being biased into its storage position, whereby said standard is pivoted into its storage position in response to tripping of said latching mechanism, and a fifth-wheel mechanism carried by the upper end of said standard and adapted to be disposed in the erected position of said standard below and in supporting relation with the front end of a cooperating semi-trailer, said fifth-wheel mechanism also being selectively operative into active and inactive positions with respect to the cooperating king pin carried by the front end of the supported semi-trailer, said fifth-wheel mechanism in its active position connecting and holding the cooperating king pin and in its inactive position disconnecting and releasing the cooperating king pin, said fifth-wheel mechanism and a connected semi-trailer being movable as a unit longitudinally of said supports effecting corresponding pivotal movements of said standard in its erected position fore-and-aft with respect to its normal upstanding attitude and longitudinally of said supports, whereby said connected device limits and cushions the movements of the connected semi-trailer longitudinally of said supports.

According to the invention there is also provided a railway car with which is combined the hitch as hereinbefore described, said railway car including a longitudinally extending frame comprising said supports and a pair of trucks supporting the opposite ends of said frame, said frame being adapted to support a trailer mounted upon the top thereof, said standard being mounted upon said frame for pivotal movements with respect thereto about an axis extending transversely thereof, said standard in said storage position disposed being closely adjacent to the top of said frame and in said erected position disposed well above the top thereof.

Accordingly the present invention furthermore provides a freight transportation system comprising a railway car including a logitudinally extending frame supported at the opposite ends thereof by a pair of trucks, a road semi-trailer including a rear end carrying road wheels and a front end carrying a king pin, a tractor carrying road wheels, a first fifth-wheel mechanism carried by the rear end of said tractor and adapted to support the front end of said trailer and selectively to couple and to uncouple said king pin, structure carried by said frame for supporting both said trailer and said tractor mounted upon the top thereof with said first fifth-wheel mechanism coupling said king pin, thereby to accommodate movements of said mounted tractor and said coupled mounted trailer longitudinally of said frame under the motive power of said mounted tractor, a standard mounted upon said frame for pivotal movements with respect thereto about an axis extending transversely thereof, said standard being selectively pivotally movable between a substantially horizontal storage position disposed closely adjacent to the top of said frame and a substantially vertical erected position disposed well above the top of said frame, latching mechanism for connecting said standard in its erected position to said frame, said latching mechanism being automatically set to latch said standard in its erected position in response to movement of said standard from its storage position into its erected position a second fifth-wheel mechanism carried by the upper end of said standard and movable therewith and adapted to be disposed in the erected position of said standard below and in supporting relation with the front end of said mounted trailer and also adapted

automatically to couple said king pin, in response to engagement thereof with said king pin, means carried by said tractor for operating said first fifth-wheel mechanism to uncouple said king pin, and additional means carried by the rear end of said tractor for pivotally moving said standard from its storage position into its erected position under the motive power of said tractor and immediately following operation of said first fifth-wheel mechanism to uncouple said king pin whereby said first fifth-wheel mechanism may be operated from said mounted tractor to uncouple said king pin and said second fifth-wheel mechanism may be moved with said standard by said mounted tractor immediately thereafter to engage said king pin so as to couple the same, thereby to effect a flying transfer of the support of the front end of said mounted trailer from said first fifth-wheel mechanism to said second fifth-wheel mechanism.

Further features of the invention pertain to the particular arrangement of the elements of the freight transportation system and of the steps of the method, whereby the above-outlined and additional operating features thereof are attained.

The invention, both as to its organization and method of operation, together with further objects and advantages thereof, will best be understood by reference to the following specification, taken in connection with the accompanying drawings, in which:

Figure 1 is a fractured side elevational view of a freight transportation system embodying the present invention and including a railway car, this figure illustrating the left-hand end of the railway car mounting an equipped road semi-trailer and including a first semi-trailer hitch supporting the front end of this mounted semi-trailer;

Figure 2 is another fractured side elevational view of the freight transportation system, this figure illustrating the right-hand end of the railway car mounting an unequipped road semi-trailer and including a second semi-trailer hitch supporting the front end of this mounted semi-trailer;

Figure 3 is an enlarged plan view, partly broken away, of the left-hand end of the railway car, taken in the direction of the arrows along the line 3-3 in Figure 1;

Figure 4 is a greatly enlarged side elevational view of the railway car, illustrating the railway bridging rail and the roadway bridging platform carried thereby, this figure being taken in the direction of the arrows along the line 4-4 in Figure 3;

Figure 5 is a greatly enlarged lateral sectional view of the railway bridging rail and the roadway bridging platform, taken in the direction of the arrows along the line 5-5 in Figure 4;

Figure 6 is an enlarged lateral sectional view of the railway car, taken in the direction of the arrows along the line 6-6 in Figure 1, and illustrating the supporting arrangement for the mounted equipped road semi-trailer;

Figure 7 is an enlarged lateral sectional view of the railway car, taken in the direction of the arrows along the line 7-7 in Figure 2, and illustrating the supporting arrangement for the mounted unequipped road semi-trailer;

Figure 8 is a diagrammatic plan view of a conventional railway flat car provided with outside wheel guide rails, and mounting an unequipped road semi-trailer, and illustrating undesirable jack-knifing tendency incident to misaligned loading of the road semi-trailer upon the railway car;

Figure 9 is a diagrammatic plan view of the inventive railway car of Figures 1 and 2 incorporating inside wheel guide rails, and mounting an unequipped road semi-trailer, and illustrating desirable centring tendency incident to misaligned loading of the road semi-trailer upon the railway car;

Figure 10 is a greatly enlarged fragmentary lateral sectional view of the railway car of Figures 1, 2 and 9, illustrating one of the roadway platforms and one of the inside wheel guide rails incorporated therein;

Figure 11 is a greatly enlarged plan view, partly broken away, of the fifth-wheel mechanism incorporated in the semi-trailer hitch, as shown in Figure 2, the jaws of this fifth-wheel mechanism being illustrated in their closed positions;

Figure 12 is a greatly enlarged longitudinal sectional view of this fifth-wheel mechanism, taken in the direction of the arrows along the line 12-12 in Figure 11;

Figure 13 is a greatly enlarged fragmentary plan view, similar to Figure 11, illustrating the jaws of this fifth-wheel mechanism in their open positions;

Figure 14 is a greatly enlarged front elevational view of this fifth-wheel mechanism, taken in the direction of the arrows along the line 14-14 in Figure 11;

Figure 15 is a greatly enlarged rear elevational view of this fifth-wheel mechanism, taken in the direction of the arrows along the line 15-15 in Figure 11,

Figure 16 is an enlarged side elevational view, partly broken away, of this fifth-wheel mechanism of Figure 11;

Figure 17 is an enlarged side elevational view, partially diagrammatic, of the railway car and the equipped road semi-trailer, as shown in Figure 1, and also illustrating the rear end of a tractor that is employed in loading the semi-trailer upon the railway car, this figure particularly illustrating the initial step in operating the cooperating semi-trailer hitch from its storage position into its erected position;

Figure 18 is another enlarged side elevational view, similar to Figure 17, partially diagrammatic, of the railway car and the equipped road semi-trailer, as shown in Figure 1, and illustrating the rear end of the tractor that is employed in loading the semi-trailer upon the railway car, this figure particularly illustrating the final step in operating the cooperating semi-trailer hitch from its storage position into its erected position and the transfer of the king pin from the fifth-wheel mechanism carried by the rear end of the tractor to the fifth-wheel mechanism carried by this hitch;

Figure 19 is an enlarged fragmentary side elevational view of this semi-trailer hitch in its erected position, as shown in Figure 18, and illustrating the extreme forward and rearward pivotal positions thereof with respect to its normal upstanding attitude, incident to shock-absorbing actions therein;

Figure 20 is a greatly enlarged fragmentary side elevational view of this semi-trailer hitch in its erected position, as shown in Figure 18, and illustrating both the latch mechanism provided in this hitch for restraining the same in its erected position and the latch mechanism provided in the fifth-wheel mechanism carried thereby, and also illustrating the cooperation between certain elements carried by the extreme rear end of the tractor and the two latch mechanisms mentioned, this figure further illustrating the latch position of the latch mechanism carried by this hitch;

Figure 21 is another greatly enlarged fragmentary side elevational view, similar to Figure 20, of the latch mechanism provided in this semi-trailer hitch, and illustrating the linkage incorporated therein immediately following tripping of the latch mechanism;

Figure 22 is a greatly enlarged fragmentary plan view of the diagonal strut incorporated in this semi-trailer hitch, taken in the direction of the arrows along the lines 22-22 in Figure 20;

Figure 23 is a greatly enlarged transverse sectional view of the diagonal strut, taken in the direction of the arrows along the line 23-23 in Figure 22;

Figure 24 is a greatly enlarged transverse sectional view of the diagonal strut, taken in the direction of the arrows along the line 24-24 in Figure 22;

Figure 25 is a greatly enlarged rear elevational view of the standard incorporated in this semi-trailer hitch, taken in the direction of the arrows along the line 25-25 in Figure 20;

Figure 26 is a greatly enlarged end elevational view, partly broken away, of the trunnion arrangement mounting one lower end of the standard, taken in the direction of the arrows along the line 26-26 in Figure 25;

Figure 27 is a greatly enlarged transverse sectional view of the standard, taken in the direction of the arrows along the line 27-27 in Figure 25.

Figure 28 is greatly enlarged fragmentary rear view of the lower portion of the mounting arrangement for the standard, as shown in Figure 25;

Figure 29 is a greatly enlarged and elevational view, partly broken away of the trunnion arrangement mounting the other lower end of the standard, taken in the direction of the arrows along the line 29-29 in Figure 28.

Figure 30 is a greatly enlarged fragmentary horizontal sectional view of one of the shock-absorbing mechanisms mounted in the centre sill of the railway car and cooperating with the semi-trailer hitch of Figures 1 and 18, this figure being taken in the direction of the arrows along the line 30-30 in Figure 18;

Figure 31 is a greatly enlarged lateral sectional view of this shock-absorbing mechanism taken in the direction of the arrows along the line 31-31 in Figure 30;

Figure 32 is an enlarged fragmentary side elevational view, similar to Figure 18, illustrating a modified form of the semi-trailer hitch, wherein the standard thereof in its erected position occupies a normal upstanding attitude that is rearwardly inclined with respect to the vertical;

Figure 33 is an enlarged fragmentary side elevational view, similar to Figure 18, illustrating another modified form of the semi-trailer hitch and incorporating an additional shock-absorbing mechanism in the vertical standard immediately below the fifth-wheel mechanism carried thereby;

Figure 34 is a greatly enlarged fragmentary side elevational view of the upper portion of the semi-trailer hitch, as shown in Figure 33;

Figure 35 is a greatly enlarged fragmentary front elevational view of the semi-trailer hitch, taken in the direction of the arrows along the line 35-35 in Figure 34;

Figure 36 is a reduced side elevational view of the freight transportation system, similar to Figures 1 and 2, and illustrating a modified form thereof, including the railway car carrying an unequipped road semi-trailer upon the left-hand end thereof and a freight container upon the right-hand end thereof;

Figure 37 is a fragmentary plan view of the rear portion of the other shock-absorbing mechanism, similar to that shown in Figure 30, that is arranged in the centre sill of the railway car and incorporating a freight container hitch;

Figure 38 is an enlarged fragmentary plan view of the underframe of the freight container, as shown in Figure 36, and illustrating the portions of the understructure that cooperate with this hitch; and

Figure 39 is a greatly enlarged transverse sectional view of the railway car, taken in the direction of the arrows along the line 39-39 in Figure 36, and illustrating the cooperation between the freight container hitch and the underframe of the freight container.

Referring now to Figures 1 and 2 of the drawings, the freight transportation system there illustrated, and embodying the features of the present invention, essentially comprises a railway car 100 of the universal type [illegible] is adapted to support and to transport individually road vehicles of first and second types. As illustrated, a road vehicle 200A of the first type is mounted on the right-hand end of the railway car 100 and a road vehicle 200B of the second type is mounted on the left-hand end of the railway car 100. Specifically, the road vehicle 200A of the first type is in the form of a road semi-trailer and essentially comprises a chassis provided with a rear end carrying road wheels 201 and a front end carrying [illegible] king pin 202 and a front [illegible] as well as a body 204 adapted to receive the cargo that is to be transported. The road vehicle 200B of the second type is also in the form of a road [illegible] and [illegible] lly of the same construction as [illegible] road vehicle 200A of the first type, except [illegible] carried at the rear end thereof dolly mechanisms hereinafter more fully indicated at 205. Accordingly, [illegible] and hereinafter the road semi-trailer [illegible] of the first type is entirely conventional and is understood that, except as [illegible] mechanisms mentioned; [illegible] road semi-trailer [illegible] of the second type is [illegible] except for the incorporation thereof [illegible] mechanisms mentioned. Thus hereinafter [illegible] of the first type is [illegible] road semi-trailer [illegible] road [illegible] some types referred to as an

Before proceeding with further description of the structural details of the trailers 200A and 200B, it is pointed out that the railway car 100 of the universal type essentially comprises, as best shown in Figures 1, 2, 3, 6 and 7, a longitudinally extending centre sill 101 of "fish-belly" construction supported at the opposite ends thereof by a pair of trucks 102 of standard rail gauge that cooperate with an associated railway track 103, also of standard rail gauge. The centre sill 101 essentially comprises a pair of longitudinally extending and laterally spaced-apart I-beams 104 that are suitably connected together at a plurality of longitudinally spaced-apart points by a corresponding plurality of cross braces 105. The top flanges 106 of the I-beams constitute a pair of longitudinally extending and laterally spaced-apart rails provided on the top of the centre sill 101 and constituting a trackway of given narrow gauge. Also the railway car 100 comprises a pair of longitudinally extending and laterally spaced-apart platforms 107 respectively carried by the outer sides of the webs of the I-beams 104 and respectively projecting outwardly therefrom and disposed below the top flanges 103 and constituting a roadway of standard road gauge. In the arrangement, and as best shown in Figures 6, 7 and 10, each of the platforms 107 is supported by a plurality of longitudinally spaced-apart and laterally outwardly projecting cantilever beams 108 disposed therebelow in supporting relation therewith, the inner ends of the beams 108 being rigidly secured, as by welding, to the outer side of the web of the adjacent I-beam 104.

Specifically, each of the platform 107 is of fabricated structure and of substantial box-like configuration, including an outer downwardly turned flange 109 and an inner upwardly turned flange 110. Also, the railway car 100 comprises a pair of longitudinally extending and laterally spaced-apart wheel guide rails 111 respectively carried upon the extreme upper ends of the upwardly directed flanges 110 provided on the inner edges of the platforms 107. As best shown in Figure 10, each of the wheel guide rails 111 is preferably of substantially tubular form and is secured, as by welding, upon the extreme upper end of the associated upwardly directed flange 110; whereby each of the wheel guide rails 111 is disposed below the adjacent rail 106 carried on the top of the associated I-beam 104 and above the top of the associated platform 107. Also, each of the wheel guide rails 111 is disposed laterally outwardly of the adjacent rail 106 and laterally inwardly of the inner edge of the associated platform 107 and presents a smooth outwardly facing rubbing surface to the adjacent inner surface of the inner road wheel 201 carried by an unequipped trailer 200A; which arrangement is utilized for a purpose more fully explained hereinafter.

As best shown in Figure 7, the unequipped trailer 200A is provided at the rear end thereof with spring mechanisms 210 carrying a pair of laterally extending tandem axles 211 that, in turn, carry the road wheels 201 on the outer ends thereof, dual road wheels 201 being illustrated for the purpose of description. When the unequipped trailer 200A is mounted upon the top of the railway car 100, the road wheels 201 directly engage the platforms 107 so that the rear axles 211 straddle the top of the centre sill 101 and are positioned above the track rails 106 and out of contact therewith, as clearly illustrated in Figure 7.

As best shown in Figure 6, the equipped trailer 200B is constructed at the rear end thereof in a manner identical to that of the unequipped trailer 200A, as shown in Figure 7, except for the provision of the previously mentioned dolly mechanisms, indicated at 220. For the purpose of the present description, the dolly mechanisms 220 have been illustrated as essentially comprising brackets 221 suitably secured to the opposite sides of the rear axles 211 in straddling relation with respect to the respectively associated spring mechanisms 210; whereby the track rollers 205 respectively carried by the brackets 221 are disposed directly below the spring mechanisms 210 and are of the previously mentioned narrow gauge of the track rails 106. When the equipped trailer 200B is mounted upon the top of the railway car 100 the track rollers 205 carried by the rear axles 211 straddle the

track rails 106 and engage the same for the purpose of supporting the rear end of the trailer 200B so as to mount the same upon the top of the centre sill 101 with the road wheels 201 projecting outwardly over the platforms 107 and positioned thereabove and out of contact therewith, as clearly illustrated in Figure 6.

Recapitulating: When the unequipped trailer 200A is mounted upon the top of the centre sill 101, the rear end thereof is directly supported by the engagements between the road wheels 201 and the platforms 107; and when the equipped trailer 200B is mounted upon the top of the centre sill 101, the rear end thereof is directly supported by the engagements between the track rollers 205 and the track rails 106.

Again referring to Figures 1 and 2, the railway car 100 carries two longitudinally spaced-apart semi-trailer hitches 300 of identical construction and arrangement, one of the hitches 300 being disposed adjacent to the left-hand end of the railway car 100, as shown in Figure 1, and normally disposed in supporting relation with the cooperating front end of the trailer 200B mounted upon the left hand end of the railway car 100, and the other of the hitches 300 being disposed adjacent to the central portion of the railway car 100, as shown in Figure 2, and normally disposed in supporting relation with the cooperating front end of the trailer 200A mounted upon the right-hand end of the railway car 100. As explained more fully hereinafter, the hitch 300 disposed in supporting relation with the front end of the trailer 200B also normally latching in place the king pin 202 thereof; and similarly, the hitch 300 disposed in supporting relation with the front end of the trailer 200A also normally latches in place the king pin 202 thereof. Accordingly, regardless of the type of the semi-trailer 200A or 200B that is mounted upon the top of the railway car 100, the front end thereof is always supported in the same manner by the cooperating hitch 300, and also regardless of the mounted position of the semi-trailer with respect to the opposite ends of the railway car 100.

A plurality of the railway cars 100 are normally arranged in a train, the adjacent ends of the railway cars being coupled together by car couplers not shown and the semi-trailers 200A and 200B are loaded indiscriminately upon the string of railway cars 100 longitudinally with respect to the train. In order to accommodate such longitudinal loading of the trailers 200A and 200B, each of the railway cars 100 comprises end structure providing both a continuous trackway and a continuous roadway along the train of railway cars 100; and this end structure that is provided at the left-hand end, of the railway car 100 is best shown in Figures 1, 3, 4 and 5. More particularly, and referring to Figure 3, the lower car rail 106 has pivotally connected thereto a bridging rail 120 and the lower car platform 111 has pivotally connected thereto a bridging platform 121. As best shown in Figures 4 and 5, the inner end of the bridging rail 120 is pivotally connected by a pivot pin 122 to the adjacent extreme outer end of the lower car rail 106 and the inner end of the bridging platform 121 is pivotally connected by a pivot pin 123 to the adjacent extreme, outer end of the lower car platform 107. The outer end of the bridging rail 120 is provided with structure 124 that is adapted to cooperate with an abutment, indicated at 125, carried by the adjacent extreme outer end of the rail structure of the coupled railway car; and the extreme outer end of the bridging platform 121 is provided with structure 126 that is adapted to cooperate with an abutment, indicated at 127, carried by the adjacent extreme outer end of the platform structure of the coupled railway car. The bridging rail 120 and the bridging platform 121 each have active positions, indicated in solid lines in Figure 4, and inactive positions, indicated in dotted lines in Figure 4; and the bridging rail 120 and the bridging platform 121 are movable together between their active and inactive positions, as explained more fully hereinafter. More particularly, when the bridging rail 120 occupies its active position, its lower position illustrated in Figure 4, the structure 124 engages the adjacent abutment 125, thereby completing a continuous rail system between the two coupled railway cars 100; and likewise, when the bridging platform 121 occupies its active position, its lower position illustrated in Figure 4, the structure 126 engages the abutment 127, thereby completing a continuous road system between the two coupled railway cars 100.

It will be understood that the right-hand end of the railway car 100 comprises end structure identical to that provided at the left-hand end of the railway car 100, except that the bridging rail and the bridging platform involved are disposed in cooperating relation with respect to the upper car rail 106 and the upper car platform 107. Accordingly, each railway car 100 carries at each end thereof end structure that is complementary to the end structure carried by either end of any other railway car 100, so that, either end of any railway car 100 may be connected to either end of another railway car 100. This will be best understood by reference to Figure 3, wherein it will be appreciated that the rail bridge 120 and the platform bridge 121 carried at the left-hand end of the railway car illustrated produces continuous rail and road systems with respect to the lower side of the right-hand end of the coupled railway car, not shown, disposed at the left of the railway car 100 illustrated; while the rail bridge indicated at 120' and the platform bridge indicated at 121' carried at the right-hand end of the coupled railway car, not illustrated, produce continuous rail and road systems with respect to the upper side of the left-hand end of the railway car 100 illustrated. Also it is noted that, as shown in Figure 3, the upper surfaces of the car platforms 107 and the upper surfaces of each of the bridging platforms 121 may carry embosses, respectively indicated at 107a and 121a, so as to provide additional frictional contact with the engaging road wheels 201 of a semi-trailer 200A or 200B, or other road vehicle, supported thereby.

Again referring to Figures 4 and 5, the bridging rail 120 and the bridging platform 121 are actuated simultaneously by an arrangement including a manually operable lever or handle 130 that is connected at the lower end thereof to a bushing 131 mounted upon a pivot pin carried by a plate 132 secured to the adjacent outer edge of the car platform 107. The bushing 131 is rigidly connected to the inner end of an arm 133, the outer end of which is connected to a tube 134 that is, in turn, connected to the underportion of the bridging platform 121 by a pair of tabs 135. Also, the bridging platform 121 is linked to the bridging rail 120 by an arrangement including a tab 136 carried by the bridging rail 120, and a link 137. One end of the link 137 is connected by a pivot pin 138 arranged in the end of the tube 134 and the other end of the link 137 is connected to the tab 136 by a spindle 139. Accordingly, when the lever or handle 130 is rotated in the clockwise direction, as viewed in Figure 4, from its position illustrated, the bushing 131 is correspondingly rotated causing the arm 133 to lift the bridging platform 121 from its active position illustrated in full lines into its inactive position illustrated in dotted lines. As the bridging platform 121 is thus rotated in the clockwise direction, as viewed in Figure 4, about the pivot pin 123, the motion is transmitted by the link 137 to the bridging rail 120 so that the bridging rail 120 is rotated in the clockwise direction about the pivot pin 122 from its active position illustrated in full lines into its inactive position illustrated in dotted broken lines. Accordingly, it will be understood that the bridging rail 120 and the bridging platform 121 may be readily moved simultaneously between their active and inactive positions by corresponding manipulations of the lever or handle 130. At this point it is mentioned that the bridging rail 120 and the bridging platform 121 occupy their lowered or active positions only during loading of the semi-trailers 200A and 200B upon the coupled railway cars 100; and after the loading operation, the bridging rail 120 and the bridging platform 121 are operated into their raised or inactive positions. It will, of course, be understood that the inactive positions of the bridging rails 120 and the bridging platforms 121 accommodate articulation of the coupled railway cars 100, without bending or other damage to these bridging elements 120 and 121.

The above-described mechanism for simultaneously actuating the bridging rail 120 and the bridging platform

121 between their respective active or use positions and their inactive or storage positions is disclosed and claimed in the copending application of Albert E. Price, Serial No 38734, filed June 13, 1960

As previously noted, the semi-trailers 200A and 200B are normally loaded longitudinally upon the railway car, and ordinarily a tractor is employed in this operation; which tractor may be either equipped or unequipped The unequipped tractor is entirely conventional, comprising a chassis provided with a front axle carrying front road wheels that are steered and a rear axle carrying rear road wheels that are driven, as well as a motor and the usual facilities. Also, the rear end of the unequipped tractor carries a conventional fifth-wheel mechanism that is selectively operative between active and inactive positions with respect to the depending king pin 202 carried by the front end of the semi-trailer 200A or 200B, the fifth-wheel mechanism in its active position supporting the front end of the semi-trailer and latching the king pin in place, and the fifth wheel mechanism in its inactive position unlatching the king pin to facilitate the removal of the semi-trailer from its supported position. The equipped tractor is identical to the above described conventional tractor, except that it further comprises low front rollers carried by the front axle and disposed inwardly with respect to the front road wheels, and also driven rear rail wheels disposed inwardly with respect to the rear road wheels. The front rollers are flanged to face inwardly so that they are adapted to straddle the track rails 106 carried on the top of the centre sill 101 of the railway car 100 and to guide thereon. The driven rear rail wheels are driven together with the rear road wheels and are also flanged to face inwardly so that they too are adapted to straddle the trace rails 106 carried on the top of the centre sill 101 of the railway car 100 and to guide thereon.

In the loading operation the fifth-wheel mechanism carried by the tractor, and regardless of the type thereof, is coupled to the king pin 202 carried by the front end of the semi-trailer 200A and 200B, and this coupled unit is backed upon the railway car 100. In the event the unequipped semi-trailer 200A is involved, the road wheels 201 thereof engage the platforms 107 and cooperate with the wheel guide rails 111 to insure centring of the semi-trailer 200A upon the top of the railway car 100 as it is backed in place thereon In the event the equipped semi-trailer 200B is involved, the low rollers 205 carried by the rear axle 211 straddle and engage the track rails 106 and guide thereon so that the road wheels 201 are disposed above the platforms 107, whereby automatic centring of the semi-trailer 200B is assured. The guiding and centring of an unequipped tractor, as it is backed upon the top of the railway car 100, is substantially identical to that of the unequipped semi-trailer 200A; and likewise, the centring and guiding of the equipped tractor, as it is backed upon the top of the railway car 100, is substantially identical to that of the equipped semi-trailer 200B.

Before describing in greater detail the centring and guiding of an unequipped semi-trailer and an unequipped tractor upon the railway car 100, reference is made to the schematic diagram of Figures 8 and 9. In Figure 8, there is illustrated a conventional railway flat car 100X that is provided with outside wheel guide rails 111X disposed along the opposite sides thereof, and there is shown diagrammatically an unequipped semi-trailer 200A mounted upon the top of the conventional railway flat car 100X, and illustrating the case wherein there is substantial misalignment between the centre line of the conventional railway car 100X and the centre line of the unequipped semi-trailer 200A. In Figure 9, there is illustrated diagrammatically an unequipped semi-trailer 200A mounted upon the top of the inventive railway car 100Y, provided with the inside wheel guide rails 111Y disposed adjacent to the centre thereof and on opposite sides of the centre line thereof, and illustrating the case wherein there is substantial misalignment between the centre line of the inventive railway car 100Y and the centre line of the unequipped semi-trailer 200A.

Referring more particularly to Figure 8, it will be observed that under the conditions mentioned, wherein there is a substantial misalignment between the centre line of the unequipped semi-trailer 200A and the centre line of the conventional railway flat car 100X, as the semi-trailer 200A is backed,one of the outside road wheels 201 thereof engages the adjacent outside guide rail 111X, thereby exerting a rotational torque upon the rear end of the semi-trailer 200A tending to cause further misalignment between the two centre lines mentioned and the resulting jack-knifing of the semi-trailer 200A with respect to the tractor, at the connection between the king pin 202 of the semi-trailer 200A and the supporting fifth-wheel mechanism carried by the rear end of the tractor. When this occurs, the driver must operate the tractor in the forward direction in order to relieve the jack-knifing mentioned; whereby the loading of the unequipped semi-trailer 200A upon the conventional flat car 100X is effected by a series of alternate rearward and forward movements of the unequipped semi trailer 200A and the coupled tractor; which operations are, of course, time-consuming and substantially injurious to the rubber of the road wheels carried by these two coupled vehicles.

Referring more particularly to Figure 9, it will be observed that under the conditions mentioned, wherein there is a substantial misalignment between the centre line of the unequipped semi-trailer 200A and the centre line of the inventive railway car 100Y,as the semi-trailer 200A is backed, one of the inside road wheels 201 thereof engages the adjacent inside guide rail 111Y, thereby exerting a rotational torque upon the rear end of the semi-trailer 200A tending to minimize the misalignment between the two centre lines mentioned and the resulting prevention of jack-knifing of the semi-trailer 200A with respect to the tractor, at the connection between the king pin 202 of the semi-trailer 200A and the supporting fifth-wheel mechanism carried by the rear end of the tractor. Since this occurs, the driver may continue to operate the tractor in the rearward direction, as the jack-knifing tendency mentioned is automatically relieved; whereby the loading of the unequipped semi-trailer 200A upon the inventive railway car 100Y is effected by a continuous rearward movement of the unequipped semi-trailer 200A and the coupled tractor; which operations are, of course, effected rapidly and without damage to the rubber of the road wheels carried by these two coupled vehicles.

With further reference to the wheel guiding and centring arrangement that is incorporated in the railway car 100, it will be observed in Figures 3 and 4 that the wheel guiding rails 111 extend substantially from end-to-end of the centre sill 101 and that each extreme outer end of each wheel guiding rail 111 is flared and curved inwardly toward the web of the adjacent I-beam 104, as indicated at 111a, thereby positively to prevent scuffing of the inside surface of the rubber of the inside road wheels 201 carried by the unequipped road semi-trailer 200A incident to loading the same upon the railway car 100 in the manner described above.

Referring now to Figures 17, 18 and 19, the semi-trailer hitch 300 that is incorporated in the left-hand end of the railway car 100 and arranged in cooperating relation with the equipped semi-trailer 200B is illustrated in greater detail; which semi-trailer hitch 300 is identical to the semi-trailer hitch 300 incorporated in the central portion of the railway car 100 and arranged in cooperating relation with the unequipped semi-trailer 200A. The semi-trailer hitch 300 illustrated essentially comprises a laterally extending trunnion 301 supported at the opposite ends thereof in the webs of the laterally spaced-apart I-beams 104 of the centre sill 101, a standard 302, and a strut 303; which hitch 300 is operative between a storage position,as shown in Figure 17, wherein it is disposed within the hollow centre sill 101 and below the top thereof, and an erected position, as shown in Figure 18, wherein it is disposed out of the hollow centre sill 101 and well above the top thereof. Also two longitudinally spaced-apart shock-absorbers 400 are incorporated in the centre sill 101 and respectively arranged in cooperating relation with the semi-trailer hitches 300. Furthermore, the upper end of the standard 302 of each of the semi-trailer hitches 300 carries a fifth-wheel

mechanism 500; and as illustrated in Figures 18 and 19, when the semi-trailer hitch 300 occupies its erected position, the fifth-wheel mechanism 500 is adapted to support the front end of the associated equipped semi-trailer 200B, the fifth-wheel mechanism 500 engaging and holding the cooperating king pin 202 depending from the front end of the semi-trailer 200B, as indicated in Figure 18. Also, when the hitch 300 occupies its erected position the rear end of the strut 303 is operatively connected to the shock-absorbing mechanism 400 by latch structure 304 that is carried by the lower end of the strut 303.

As best shown in Figures 20 and 25 to 29, inclusive, the trunnion 301 is of generally tubular form, and the standard 302 comprises a pair of laterally spaced apart legs 305, each of substantially box-like form, as shown in Figure 27, and rigidly secured to the intermediate portion of the trunion 301, as by welding. Also, the connections between the lower ends of the legs 305 and the trunnion 301 are reinforced by suitable gusset plates 306 secured in place, as by welding, between the lower ends of the legs 305 and the trunnion 301. Further, the outer ends of the trunnion 301 are reinforced adjacent to the lower portions thereof by suitable gusset plates 307, so as to lend the required rigidity to the trunnion 301. The upper portions of the legs 305 are rigidly secured together by a laterally extending pivot pin 308, to which the upper end of the strut 303 is pivotally connected, as explained more fully hereinafter; also, the lower ends of the legs 305 are rigidly secured together by a tie plate 309 that is further secured to the adajcent central portion of the trunnion 301. Further, the front sides of the legs 305 carry forwardly projecting ears 310 between which there is rigidly secured a hook shaft 311 (see Figures 20, 25 and 28), that is employed in operating the hitch 300 from its storage position of Figure 17 into its erected position of Figure 18. The upper ends of the legs 305 taper outwardly, as illustrated in Figure 25; and the extreme upper ends of the legs 305 carry a pair of laterally spaced-apart lugs 312 to which the associated fifth-wheel mechanism 500 is pivotally connected, as explained more fully hereinafter

Referring now to Figures 25 to 29, inclusive, the opposite ends of the trunnion 301 terminate respectively adjacent to the inside surfaces of the webs of the associated I-beams 104 and are respectively supported for pivotal movements by associated bearing structures 313 and 314 located between the upper and lower flanges of the respectively associated I-beams 104. As viewed in Figure 28, the bearing structure 313 is arranged at the left-hand end of the trunnion 301 and the bearing structure 314 is arranged at the right-hand end of the trunnion 301; whereby the standard 302 is disposed between the upper flanges or track rails 106 of the I-beams 104 of the centre sill 101, so that the standard 302 may be readily pivoted between its stored and erected positions, as previously noted, without interference with the I-beams 104. More particularly, the bearing structure 313 comprises a supporting ring 315 that is rigidly secured to the adjacent inner surface of the web of the associated I-beam 104 by a plurality of gusset plates 316; which supporting ring 315 receives a bearing ring 317 internally thereof and arranged for rotary movements with respect thereto; which bearing ring 317 is arranged in surrounding relation with the adjacent left-hand end of the trunnion 301 with a resilient cushioning ring 318 therebetween. Preferably the cushioning ring 318 is formed of neoprene, or other resilient rubber-like material, and is bonded to the adjacent inner surface of the bearing ring 317 and to the adjacent outer surface of the left-hand end of the trunnion 301. Similarly, the bearing structure 314 comprises a supporting ring 319 that is rigidly secured to the adjacent inner surface of the web of the associated I-beam 104 by a plurality of gusset plates 320, which supporting ring 319 receives a bearing ring 321 internally thereof and arranged for rotary movements with respect thereto; which bearing ring 321 is arranged in surrounding relation with the adjacent right-hand end of the trunnion 301 with a resilient cushioning ring 322 therebetween. Preferably, the cushioning ring 322 is formed of neoprene, or other resilient rubber-like material, and is bonded to the adjacent inner surface of the bearing ring 321 and to the adjacent outer surface of the right-hand end of the trunnion 301.

Accordingly, it will be appreciated that the bearing structures 313 and 314 not only support the trunnion 301 for pivotal movements between the webs of the associated laterally spaced-apart I-beams 104, but they also provide a resilient mounting between the trunnion 301 and the I-beams 104, thereby effecting cushioning of the standard 302 in its erected position, for a purpose more fully explained hereinafter.

Still referring to Figure 28, a pair of aligned openings 323 are respectively formed in the webs of the laterally spaced-apart I-beams 104 in alignment with the opposite ends of the tubular trunnion 301; and arranged within the tubular trunion 301 and extending laterally therethrough is a torsion member 324 that essentially comprises a plurality of individual leaf springs 325 arranged in stacked relation, as best illustrated in Figures 26 and 29. Referring now to Figures 28 and 29, a pair of abutments 326 are arranged in the outer left-hand end of the tubular trunnion 301 and rigidly secured thereto; which abutments 326 are disposed on opposite sides of the adjacent left-hand end of the torsion member 324; whereby the left hand end of the torsion member 324 rotates directly with the adjacent left-hand end of the trunnion 301 incident to rotation of the trunnion 301 in the bearing structures 313 and 314. Referring now to Figures 28 and 26, a cap 327 is arranged on the outer side of the web of the I-beam 104 disposed on the right-hand side of the centre sill 101, as viewed in Figure 26; which cap 327 carries an upwardly projecting tab 328 arranged between a pair of outwardly projecting ears 329 rigidly secured to the adjacent outer surface of the adjacent web of the I-beam 104; and the tab 328 is mounted upon the ears 329 for pivotal movement with respect thereto by an associated pivot pin 330. Thus it will be understood that the cap 327 is pivotally movable with respect to the associated web of the I-beam 104 about the pivot pin 330, thereby to afford access to the adjacent right-hand end of the torsion member 324, when the cap 327 occupies its open position with respect to the associated opening 323. Further, a substantially U-shaped retainer 331 is disposed below the cap 327 and rigidly secured to the adjacent surface of the web of the I-beam 104; which retainer 331 restrains the cap 327 against longitudinal movements from side to side, as viewed in Figure 26. Arranged within the cap 327 are a pair of abutments 332 that are rigidly secured thereto and disposed on opposite sides of the adjacent right-hand end of the torsion member 324.

When the standard 302 occupies its erected position, the torsion member 324 is unstrained and may be removed from its normal position within the trunnion 301 through the opening 323 provided in the web of the adjacent I-beam 104 in the left-hand end of the trunnion 301, as viewed in Figure 28, after removal of an associated cover 333 carried by the adjacent web of the I-beam 104 and normally secured in place by a bolt 334 provided with an associated nut. Accordingly, when the standard 302 occupies its erected position, the unstrained torsion member 324 extends laterally through the trunnion 301, the left hand end of the torsion member 324 being disposed between the associated abutments 326 rigidly secured to the trunnion 301 and the right-hand end of the torsion member 324 projecting through the opening 323 provided in the web of the associated I-beam 104 and into the cap 327 and disposed between the abutments 332 rigidly secured thereto. As the standard 302 is moved from its erected position, as shown in Figure 18, toward its storage position, as shown in Figure 17, the trunnion 301 is rotated in the clockwise direction causing the abutments 326 arranged in the left-hand end thereof to twist the left-hand end of the torsion member 324 in the clockwise direction, as viewed in Figure 29, so that the right-hand end of the torsion member 324 is rotated in the counterclockwise direction, as viewed in Figure 26. The initial counterclockwise rotation of the torsion member 324, as viewed in Figure 26, is unopposed; however, after

rotation of the torsion member 324 through a predetermined angle in the counterclockwise direction, the right-hand end thereof engages the abutments 332 that are arranged in the cap 327 and rigidly secured thereto, whereby the torsion member 324 is strained as the left-hand end thereof is rotated further in the clockwise direction, as viewed in Figure 29, since the right-hand end of the torsion member 324 cannot be rotated further in the counterclockwise direction, as viewed in Figure 26, as the cap 327 is fixedly secured to the web of the adjacent I-beam 104 by the arrangement including the ears 329 and the retainer 331, as shown in Figure 26. Accordingly, as the standard 302 is pivoted in the clockwise direction from its erected position of Figure 18, into its storage position of Figure 17, the torsion member 324 is strained, or twisted between the pair of abutments 326 and the pair of abutments 332, so as to store energy in the torsion member 324 as the standard 302 is pivoted into its final storage position, as shown in Figure 17. Of course, this straining of the torsion member 324 is productive of a reactive force between the cap 327 and the left-hand end of the trunnion 301, as viewed in Figure 28, thereby opposing the final pivotal movement of the standard 302 into its storage position, as shown in Figure 17; which reactive force, tending to move the standard 302 from its storage position of Figure 17 back into its erected position of Figure 18, minimizes the torque that must be exerted from the outside upon the hitch 300 in order to move the same from its storage position of Figure 17 into its erected position of Figure 18.

Referring now to Figures 20 to 24, inclusive, and 31, the strut 303 is of substantially box-like form including a pair of side plates 335, a bottom plate 336, a lower top plate 337 and an upper top plate 338. The upper ends of the side plates 335 are inwardly offset toward each other, so that the upper end of the strut 303 is substantially narrower in the lateral direction than is the lower end thereof; the upper end of the strut 303 terminates in a laterally extending hollow bearing 339 that is journalled upon the pivot pin 308 extending between the legs 305 of the standard 302; and the lower end of the strut 303 terminates in respective lower and upper laterally extending tubular members 340 and 341 (see particularly Figure 20). The upper tubular member 341 is rigidly secured to the lower tubular member 340 by an associated gusset plate 342, and the upper tubular member 341 is rigidly secured to the lower top plate 337 by an associated gusset plate 343; whereby the lower end of the strut 303 carries the tubular members 340 and 341 rigidly secured thereto. The upper tubular member 341 constitutes a bearing member in which there is journalled a laterally extending supporting shaft 344; and the opposite ends of the supporting shaft 344 carry a pair of slides 345 that are resectively arranged in a pair of trackways 346 respectively carried by the pair of laterally spaced-apart I-beams 104.

As best shown in Figures 20 and 31, each of the trackways 346 is located adjacent to the junction between the upper portion of the web of the associated I-beam 104 and the upper flange 106 thereof and below the inwardly directed projection of the upper flange 106 thereof; and each of the trackways 341 comprises an upper rail element 347 and a lower rail element 348. The upper rail element 347 may be secured directly to the undersurface of the inwardly directed projection of the upper flange 106, and each of the lower rail elements 347 may be supported by a suitable number of longitudinally spaced apart gusset plates 349 directly secured to the inner surface of the web of the associated I-beam 104. Finally, the rail elements 347 may be secured together in vertical spaced-apart relationship by a number of longitudinally spaced-apart bocks 350 arranged therebetween.

Accordingly, it will be understood that the upper end of the strut 303 is pivotally connected to the intermediate portion of the standard 302 by the cooperation between the pivot pin 308 and the bearing member 339; while the lower end of the strut 303 is supported by the pair of slides 345 arranged in sliding engagements with the pair of laterally spaced-apart trackways 346 respectively carried by the laterally spaced-apart I-beams 104 of the centre sill 101. Thus the movements of the standard 302 between its storage position of Figure 17 and its erected position of Figure 18 are guided upon the centre sill 101, and particularly through the strut 303 by the sliding movements of the shoes 345 along the trackways 346. More specifically, when the standard 302 is moved from its erected position, as shown in Figure 20, the lower end thereof is pivoted in the clockwise direction with the trunnion 301; whereby the lower end of the strut 303 moves toward the right, this movement of the strut 303 being guided by the cooperation between the shoes 345 and the cooperating trackways 346.

Referring now to Figures 20, 22 and 30, the lower tubular member 340 carried by the lower end of the strut 303 constitutes a bearing member for a laterally extending shaft 351 that comprises a portion of the previously mentioned latch structure 304. More particularly, the latch structure 304 comprises a pair of laterally spaced-apart latch elements 352 rigidly secured to the extreme outer ends of the shaft 351, the latch elements 352 being disposed outwardly of the respectively adjacent side plates 335 of the strut 303, as shown in Figure 22. As illustrated, the two latch elements 352 project forwardly with respect to the shaft 351 and are normally biased downwardly in the counterclockwise direction, with respect to the strut 303, as viewed in Figure 20, by a pair of cooperating laterally spaced-apart coil springs 353. Each of the coil springs 353 cooperates with one of the latch elements 352, one end of the coil spring 353 being arranged in an associated cup 354 rigidly secured to the adjacent side plate 335 of the strut 303, and the other end of the coil spring 353 being received in a recess 352a provided in the upper surface of the adjacent latch element 352 (see Figure 30). Each of the latch elements 352 carries a downwardly directed latch portion or dog 356 having set and trip positions with respect to the associated shock-absorbing mechanism 400, as explained more fully below.

Referring now to Figures 20, 30 and 31, the shock-absorbing mechanism 400 that cooperates with the associated hitch 300 essentially comprises two longitudinally extending and laterally spaced-apart shafts 401 respectively arranged adjacent to the webs of the associated I-beams 104 of the centre sill 101 and generally positioned rearwardly of the cooperating lower end of the strut 303 of the hitch 300. More particularly, the shock-absorbing mechanism 400 is housed within the hollow centre sill 101, and each of the longitudinally extending shafts 401 is mounted for longitudinal sliding movements with respect to the associated I-beam 104. As illustrated, each of the shafts 101 is mouted for longitudinal movements in a pair of longitudinally spaced-apart brackets 402 carried by the web of the associated I-beam 104 and projecting inwardly with respect thereto. The intermediate portion of the shaft 401 carries a stack of resilient snubbing rings 403 arranged in surrounding relation with respect thereto and disposed between the brackets 402; which snubbing rings 403 are preferably formed of neoprene, or other resilient cushioning material. Specifically, the snubbing rings 403 are disposed in stacked relation between two longitudinally spaced-apart annular collars 404 arranged in surrounding relationship with respect to the shaft 401 and disposed adjacent to the respective brackets 402. The rear ends of the shafts 401 are operatively connected together by a laterally extending rear tie bar 405, and the front ends of the shafts 401 are operatively connected together by a laterally extending front tie bar 406, the tie bars 405 and 406 being removably secured in place by cooperating nuts 407 and 408 arranged on the threaded rear and front ends of the shafts 401. In the arrangement the front tie bar 406 cooperates with the pair of latch elements 352 carried by the lower end of the strut 303 of the hitch 300; and specifically, the latch elements 352 are operative into set and trip positions with respect to the front tie bar 406, as respectively shown in Figures 20 and 21, and explained more fully hereinafter.

It will be understood that when the front tie bar 406 is moved rearwardly, or to the right, with respect to the centre sill 101, the rearwardly moving shafts 401 compress the two stacks of snubbing rings 403 between the left-hand collars 404 and the right-hand brackets 402;

and conversely, when the tie bar 406 is moved forwardly, or to the left, with respect to the centre sill 101, the forwardly moving shafts 401 compress the two stacks of snubbing rings 403 between the right-hand collars 404 and the left-hand brackets 402. Accordingly, the mechanism 400 not only resiliently opposes the movements of the front tie bar 406 with respect to the normal position thereof, as illustrated in Figure 20, but it also snubs these movements and dissipates the energy thereof; which snubbing action is, of course, transmitted to the adjacent hitch 300, when the latch structure 304 occupies its set position.

Again referring to Figures 18 and 20, when the standard 302 is pivoted in the counterclockwise direction from its storage position, as shown in Figure 17, into its erected position, as shown in Figure 18, the strut 303 moves to the left and into an upwardly inclined position, as shown in Figure 18; whereby the latch elements 352 carried by the rear end of the strut 303 slide over the front tie bar 406 and into their latched positions, as shown in Figures 18 and 20; whereby at this time, the lower end of the strut 303 is latched to the adjacent shock-absorbing mechanism 400, thereby to retain the hitch 300 in its erected position. In the erected position of the hitch 300, the standard 302 is biased by the connected shock-absorbing mechanism 400 into a normal upstanding attitude, as shown in Figure 18, and as indicated by the vertically disposed centre line 357, as shown in Figure 19. At this time, the standard 302 is pivotally movable with the trunnion 301 fore-and-aft with respect to its normal upstanding attitude and longitudinally of the centre sill 101 between the extreme forward position, indicated by the centre line 358, and the extreme rearward position, indicated by the centre line 359, as shown in Figure 19. These pivotal movements of the standard 302 in its erected position are, of course, transmitted thereto through the fifth-wheel mechanism 500 by the connected equipped semi-trailer 200B, incident to rolling movements of the connected semi-trailer 200B longitudinally of the centre sill 101; and these pivotal movements of the standard 302 are transmitted by the strut 303 to the front tie bar 406 of the shock-absorbing mechanism 400; whereby the pivotal movements mentioned are cushioned and limited by the shock-absorbing mechanism 400 effecting corresponding cushioning and limiting of the movements of the semi-trailer 200B. More particularly, as shown in Figure 19, when the standard 302 occupies its normal upstanding attitude disposed along the centre line 357, the front tie bar 406 occupies its normal position disposed along the centre line 360; as the standard 302 is pivoted forwardly into the position of the centre line 358, the front tie bar 406 is moved forwardly to the position of the centre line 361; and as the standard 302 is pivoted rearwardly into the position of the centre line 359, the front tie bar 406 is moved rearwardly to the position of the centre line 362. From a comparison of the positions of the centre lines 357, 358 and 359 with the centre lines 360, 361 and 362, it will be appreciated that the movements of the upper end of the standard 302, and consequently of the fifth-wheel mechanism 500 carried thereby, are increased or multiplied with respect to the movements of the front tie bar 406, due to the mechanical advantage of the linkage of the elements incorporated in the hitch 300. In view of the foregoing, it will be appreciated that the shock-absorbing mechanism 400 prevents the transmission of severe longitudinal shocks from the centre sill 101 of the railway car 100 to the equipped semi-trailer 200B connected to the hitch 300 and mounted upon the top of the centre sill 101.

Again referring to Figures 20 and 21, it is noted that tripping mechanism is incorporated in the hitch 300 for the purpose of selectively operating the latch structure 304 from its latched position, as shown in Figure 20, into its unlatched position, as shown in Figure 21. More particularly, a cam 363 is arranged between the laterally spaced-apart latch elements 352 and is pivotally mounted upon a pivot pin 364 extending between the latch elements 352. A pair of laterally spaced-apart ears 365 are carried by the lower end of the strut 303 and connected together by a pivot pin 366; and a lever 367 is pivotally mounted upon the pivot pin 366 and arranged in an opening provided in the bottom plate 336 of the strut 303 and adjacent to the cam 363. A link 368 is connected between a pivot pin 369 carried by the cam 363 and a pivot pin 370 carried by the lever 367. A pair of laterally spaced-apart ears 371 carried by the upper end of the strut 303 and connected together by a laterally extending pivot pin 372, upon which there is mounted a lever 373. The lower end of the lever 373 is connected by a pivot pin 374 to a fixture 375 that is connected to the upper end of a tie bar 376; and the lower end of the tie bar 376 is connected to a fixture 377 that is connected by a pivot pin 378 to the lever 367. A barrel 379 is secured to the upper end of the standard 302 above the pivot pin 305; and arranged within the barrel 379 is a plunger 380 that is mounted for sliding movement with respect thereto, the outer end of the plunger 380 terminating in a strike button 381, and the plunger 380 being biased toward the left, as viewed in Figure 20, by a surrounding coil spring 382 acting between the adjacent ends of the barrel 379 and the strike button 381. The right-hand end of the plunger 380 carries a fixture 383 that is secured by a pivot pin 384 to the upper end of the lever 373. Accordingly, the cam 363 is operatively connected to the strike button 381 through the linkage above described; and moreover, the cam 363 is biased into its position, as shown in Figure 20, through the linkage described by the coil spring 382.

In order to operate the cam 363 so as to effect lifting of the latch elements 352 in the clockwise direction about the pivot pin 351, as viewed in Figure 20, and the consequent operation of the latch elements 352 into their unlatching positions with respect to the front tie bar 403 and into the positions as illustrated in Figure 21, the strike button 381 is operated or moved from its extended position, as shown in Figure 20, toward the right, as shown in Figure 21. This movement of the strike button 381 toward the right is against the bias of the coil spring 382, whereby the plunger 380 is moved toward the right with respect to the barrel 379, thereby moving the fixture 383 toward the right, causing the lever 373 to be rotated in the clockwise direction about the pivot pin 372, with the result that the fixture 375 is lifted upwardly moving the tie bar 376 upwardly. The upward movement of the tie bar 376 rotates the lever 367 in the counterclockwise direction, as viewed in Figure 20, lifting the link 368 upwardly, so that the cam 363 is rotated in the clockwise direction, as viewed in Figure 20; whereby the lower curved end thereof cams against the top surface of the front tie bar 406, lifting the latch elements 353 upwardly from their latching positions of Figure 20 into their unlatching positions of Figure 21. Also, at this time, the force that is exerted upon the strike button 381, following operation of the latch elements 352 into their unlatching positions of Figure 21, effects clockwise rotation of the standard 302 with the trunnion 301; whereby the hitch 300 is moved from its erected position of Figure 18 back into its storage position of Figure 17, since the hitch 300 is gravity-biased into its storage position.

Of course, after the force is removed from the strike button 381, the coil spring 382 returns the strike button 381 and the remainder of the linkage back into the positions, as illustrated in Figure 20, with the result that the cam 363 is returned back into its normal position; however, at this time, the lower end of the strut 303 has moved rearwardly, guided by the sliding engagements between the shoes 345 and the trackways 346; whereby the hitch 300 in its storage position is operatively disconnected from the associated shock-absorbing mechanism 400, as clearly illustrated in Figure 17.

Considering now the construction and arrangement of the fifth-wheel mechanism 500 and referring to Figures 11 to 16, inclusive, this mechanism essentially comprises a head in the form of a top plate 501 defining a table adapted to engage the reinforced understructure of the front end of either an unequipped semi-trailer 200A or an equipped semi-trailer 200B; which top plate 501 is provided with a pair of laterally spaced apart and downwardly directed side aprons 502 extending longitudinally of the centre sill 101 of the railway car 100; which side

aprons 502 are pivotally connected adjacent to the front ends thereof, the left-hand ends thereof, as viewed in Figure 11, to the outwardly directed lugs 312 carried by the upper ends of the legs 305 of the standard 302 by an arrangement including a pair of pivot pins 503. More particularly, a pair of longitudinally extending and laterally spaced-apart plates 504 are respectively arranged inwardly of the side aprons 502 and in spaced relation therewith, the upper edges of the plates 504 being suitably secured, as by welding, to the lower surface of the top plate 501. The plates 504 lend additional rigidity to the structure and respectively receive the inner ends of the previously mentioned pivot pins 503. In this arrangement, each of the pivot pins 503 is disposed within a cylindrical bearing element 505 that extends through aligned openings provided in the adjacent side apron 502 and in the adjacent plate 504, the inner end of the pivot pin 503 having an opening therein through which a cotter key 506 is arranged. Accordingly, the head of the fifth wheel mechanism 500 is mounted upon the lugs 312 carried by the upper ends of the legs 305 of the standard 302 for pivotal movements about the aligned pivot pins 503; and the head is normally restrained in a position disposed substantially normally to the standard 302, as shown in Figure 16, by arrangement including a pair of laterally spaced-apart and longitudinally extending leaf springs 507 acting between the lugs 312 on the standard 302 and the undersurface of the top plate 501. More particularly, as illustrated in Figure 16 each of the leaf springs 507 is substantially L-shaped, including a short downwardly directed leg 507a wrapped over the adjacent lug 312 on the standard 302 and secured in place by an associated screw 508 and a long rearwardly extending leg 507b arranged immediately below the undersurface of the top plate 501 and in engagement therewith.

Further, the head of the mechanism 500 comprises a rear plate 509, disposed at the right-hand side of Figure 11, and a bottom plate 510 spaced below the top plate 501 and cooperating therewith to provide a hollow box-like structure having an open front end disposed at the left of Figure 11. Also, a guide slot 511 is formed in the central front portion of the top plate 501 and having rearwardly converging side walls terminating in a substantially semi-circular recess 512 disposed adjacent to the longitudinal centre line of the top plate 501 and rearwardly of the front edge thereof; which recess 512 defines a home position for the cooperating depending king pin 202 carried by the front end of an associated semi-trailer 200A, etc.

The lower central portion of the top plate 501 is reinforced by a top block 513 disposed therebelow and positioned forwardly above the bottom plate 510; the top block 513 and the bottom plate 510 are suitably secured in assembled relation with the top block 513 spaced above the bottom plate 510. Also, the top block 513 has a guide slot formed in the front central portion thereof that generally conforms to the guide slot 511 formed in the top plate 501, as well as a centrally disposed semi-circular recess at the rear central portion thereof that generally conforms to the semi-circular recess 512 formed in the top plate 501.

A pair of laterally spaced-apart and vertically disposed pivot pins 514 are arranged on opposite sides of the semi-circular recess 512 and extend through the top block 513 and the bottom plate 510; and upon the pivot pins 514 a pair of locking members 515 are respectively pivotally mounted intermediate the ends thereof. Each of the locking members 515 comprises, as best shown in Figure 13, a forwardly directed protuberance 516 and an inwardly directed centrally disposed protuberance 517 cooperating to define a forwardly directed substantially semi-circular locking jaw 518; and also each of the locking members 515 comprises a rearwardly directed cam element 519. Accordingly, the locking elements 515 are pivotally mounted upon the pivot pins 514 between the upper block 513 and the lower plate 510 and are movable between locking and unlocking positions with respect to a cooperating king pin 202, indicated in broken lines in Figure 11.

Also arranged between the top block 513 and the bottom plate 510 are rearwardly of the locking members 515 is guide structure including a pair of longitudinally extending and laterally spaced-apart guide members 520 and a connecting bridge member 521; and arranged between the guide members 520 and fowardly of the bridging member 521, there is disposed a locking block 522. The locking block 522 is located rearwardly of the locking members 515 and forwardly of the bridging member 521 and is mounted for longitudinal sliding movements upon the bottom plate 510 along the longitudinal axis of the head of the mechanism 500. A centrally disposed opening 523 is arranged in the bridging member 521 that is covered by an associated hollow cap 524; and within the cap 524 there is arranged a compression spring 525. As viewed in Figure 13, the rear end of the compression spring 525 bears against the end of the cap 524 and the front end of the compression spring 525 is arranged in a recess 522a provided in the rear end of the locking block 522; whereby the compression spring 525 biases the locking block 522 forwardly, or toward the left, as viewed in Figure 13, into engagement with the cams 519 carried by the rear ends of the locking members 515.

When the locking members 515 occupy their unlocking positions, as shown in Figure 13, the locking jaws 518 are open and are adapted to receive a cooperating king pin 202 when moved longitudinally rearwardly thereinto and the cams 519 engage the locking block 522; whereby the locking block 522 restrains the locking members 515 in their unlocking positions illustrated, by frictional engagement. At this time, in the event a king pin 202 is moved longitudinally rearwardly between the locking jaws 518, it will pass between the front protuberance 516 carried by the locking members 515 and will engage the centrally disposed protuberances 517 as it arrives in its home position in the semi-circular recess 512 provided in the top plate 501; whereby the engagements of the king pin 202 with the central protuberances 517 rotates the locking members 515 about the pivot pins 514 to spread the cams 519 away from each other, as viewed in Figure 13, so that the cams 519 ride over the adjacent corners at the front end of the locking block 522, with the result that the compression spring 525 projects the locking block 522 fowardly between the cams 519 and into its locking position, shown in Figure 11. At this time, the king pin 202 is firmly gripped between the locking jaws 518 in its home position in the semi-circular recess 512 provided in the top plate 501 and is retained in place by virtue of the fact that the locking block 522 is now projected between the cams 519 provided at the rear ends of the locking members 515.

Also, as best illustrated in Figures 12 and 13, the locking jaws 518 provided on the front end of the locking members 515 are contoured to define a cavity 518a at the lower portions thereof disposed closely adjacent to the top surface of the bottom plate 510, so as to conform to the normal shape of the king pin 202. More particularly, the depending king pin 202 carried by the front end of a semi-trailer 200A or 200B normally comprises an enlarged head that is supported by the top surface of the bottom plate 510 in the home position thereof in the semi-circular recess 512 provided in the top plate 501; whereby the locking jaws 518 grip the shank of the cooperating king pin 202, as well as the enlarged head thereof disposed in the cavities 518a, as noted above.

As best shown in Figures 12 and 13, the rear end of the block 522 carries a depending tab 526 that is disposed in a cooperating centrally disposed and longitudinally extending slot 510a provided in the bottom plate 510; whereby the tab 526 projects downwardly below the bottom plate 510. A longitudinally extending and centrally disposed plunger 527 is mounted below the plate 510 upon a number of depending elements 528, 529 and 530 carried thereby; and the rear end of the plunger 527 is connected to the tab 526. The front end of the plunger 527 projects forwardly of the front end of the head of the mechanism 500 and terminates in a strike button 531 that is secured in place thereupon by an associated cotter key 532. More particularly, the plunger 527 is mounted in cooperating openings provided in the elements 528, 529 and 530 for sliding movements longitudinally of the

bottom plate 510, thereby to effect corresponding sliding movements of the connected locking block 522 with respect to the cams 519 carried at the rear ends of the locking members 515.

When the locking jaws 518 carried by the locking members 515 occupy their locking positions, as illustrated in Figures 11 and 12, the locking block 522 occupies its forwardly projected position, as previously explained; whereby the plunger 527 occupies its forwardly projected position, also illustrated in Figures 11 and 12, the locking block 522 and the plunger 527 being moved into their forward positions by the compression spring 525. At this time, in the event the strike button 531 is struck a blow and moved rearwardly toward the right, as viewed in Figures 11 and 12, the plunger 527 is moved rearwardly causing the locking block 522 to move rearwardly against the bias of the compression spring 525 so that the locking block 522 is moved from between the cams 519 in order to accommodate rotational movements of the locking members 515 to move the locking jaws 518 into their unlocking positions with respect to the associated king pin 202, as shown in Figure 13.

Reconsidering the operation of the hitch 300 and the method of loading the equipped semi-trailer 200B onto the top of the railway car 100, reference is again made to Figures 17 and 18, and it is assumed that at this time, the hitch 300 occupies its storage position, as illustrated in Figure 17. In this loading operation, a tractor 600 partially illustrated in Figures 17 and 18, is employed; and the rear end of the chassis of the tractor 600 is indicated at 601 as being supported by rear road wheels 602; and also, it is assumed that the tractor 600 is of the unequipped type, so that the road wheels 602 thereof are supported upon the road platforms 107 carried on the opposite sides of the centre sill 101 of the railway car 100, in the manner previously explained. Also, the rear end of the chassis 601 carries a conventional fifth-wheel mechanism 603 that is adapted to support the front end of the associated semi-trailer 200B and selectively to lock and to unlock the king pin 202 thereof. The fifth-wheel mechanism 603 is arranged automatically to receive and to lock the associated king pin 202, and the fifth-wheel mechanism 603 may be operated into unlocking relation with respect to the king pin 202 through an associated control cable 604 that may be governed from the cab, not shown, of the tractor 600. Also the rear end of the chassis 601 carries a pivotally mounted link 605 that, in turn, carries a pivotally mounted hook 606; which link 605 and hook 606 may be suitably operated through an associated control cable 607 that may be governed from the cab of the tractor 600. Further, the rear end of the chassis 601 carries two centrally disposed and longitudinally spaced-apart stops or abutments 608 and 609 that are arranged respectively to cooperate with the strike buttons 531 and 381 respectively carried by the fifth-wheel mechanism 500 and by the hitch 300, as indicated in Figure 20. This arrangement is described more fully below, but, at this time, it is noted that the abutment 608 is disposed more rearwardly than is the abutment 609, so that the abutment 608 first strikes the strike button 531 and immediately thereafter, the abutment 609 strikes the strike button 381.

Returning now to the method of loading the equipped semi-trailer 200B upon the top of the railway car 100 and again referring to Figure 17, the king pin 202 of the semi-trailer 200B is coupled to the fifth-wheel mechanism 603 carried by the rear end of the chassis 601 of the tractor 600, while the semi-trailer 200B and the tractor 600 are in the freight yard associated with the railway track 103, upon which the railway car 100 is standing. The tractor 600 draws the coupled semi-trailer 200B to the vicinity of the adjacent front end of the railway car 100 and then backs the semi-trailer 200B rearwardly onto the top of the railway car 100, with the rail bridging member 120 and the platform bridging member 121 in their lower positions, in the manner previously explained; whereby the semi-trailer 200B and then the tractor 600 are backed upon the adjacent left-hand end of the railway car 100, the rear end of the semi-trailer 200B being supported by the engagements between the track rollers 205 and the track rails 106 carried by the top of the I-beams 104 and the road wheels 602 of the tractor 600 engaging the platforms 107 carried by the opposite sides of the centre sill 101 of the railway car 100, in the manner previously explained.

More particularly, the semi-trailer 200B is backed over the hitch 300 in its storage position, as shown in Figure 17 and so that the hook 606 carried by the rear end of the chassis 601 of the tractor 600 is disposed above the hook shaft 311 carried by the standard 302 of the hitch 300. The control cable 607 is manipulated from the cab of the tractor 600, so as to lower the link 605 and the hook 606 in order to cause the hook 606 to engage the hook shaft 311, as illustrated in Figure 17. At this time, the tractor 600 and the coupled semi-trailer 200B is moved forwardly under the motive power of the tractor 600, so that the hook 606 pulls forwardly upon the hook shaft 311 causing the standard 302 to pivot in the counterclockwise direction about the trunnion 301, as viewed in Figure 17; whereby the standard 302 is pivoted upwardly and into an upstanding position disposed behind the rear end of the chassis 601 positioning the fifth-wheel mechanism 500 behind the fifth-wheel mechanism 603. At this time, the control cable 604 is actuated in order to operate the fifth-wheel mechanism 603 so as to uncouple the king pin 202 carried by the front end of the semi-trailer 200B while the tractor 600 is driven forwardly pivoting further the standard 302 into its normal upstanding attitude. The tractor 600 is then driven further forwardly so as to pivot the standard 302 into its fully upstanding attitude; whereby the hitch 300 is operated into its fully erected position, as shown in Figure 18, so that the fifth-wheel mechanism 603 is moved from under the front end of the semi-trailer 200B and the fifth-wheel mechanism 500 is moved immediately thereafter under the front end of the semi-trailer 200B. At this time, the fifth-wheel mechanism 500 operates automatically to receive the king pin 202 of the semi-trailer 200B and to lock the same in place; and also the latch structure 304 is operated into its latched position with respect to the front tie bar 406 of the shock-absorbing mechanism 400. The tractor 600 is then backed up slightly so as to disengage the hook 606 from the hook shaft 311; and the control cable 607 is actuated from the cab of the tractor 600 so as to raise the link 605 and the hook 606 back into their normal elevated positions. At this time, the tractor 600 is completely disconnected from the hitch 300; the hitch 300 occupies is erected position; and the fifth-wheel mechanism 500 supports the front end of the semi-trailer 200B and locks in place the king pin 202 of the semi-trailer 200B. Accordingly, the front end of the semi-trailer 200B is connected to the fifth-wheel mechanism 500 and the hitch 300 in its erected position is operatively connected to the shock-absorbing mechanism 400. Of course, the tractor 600 is then driven off of the left-hand end of the railway car 100 to be employed in further loading operations. In view of the foregoing, it will be understood that a flying transfer is made of the support of the front end of the semi-trailer 200B from the fifth-wheel mechanism 603 carried by the rear end of the chassis 601 of the tractor 600, to the fifth-wheel mechanism 500 carried by the upper end of the standard 302 of the hitch 300 carried by the railway car 100, with a continuous forward movement of the tractor 600 along the top of the railway car 100.

As previously explained, during the operation of the railway car 100, the semi-trailer 200B is mounted upon the top thereof and is capable of limited longitudinal rolling movements therealong; which longitudinal movements of the semi-trailer 200B and the connected fifth-wheel mechanism 500 take place together, and as a unit, imparting corresponding fore-and-aft movements to the hitch 300 and the consequent transmission of such fore-and-aft movements to the shock-absorbing mechanism 400; whereby the shock-absorbing mechanism 400 absorbs the severe longitudinal shocks effecting cushioned and limited longitudinal movements of the semi-trailer 200B in its mounted position upon the top of the railway car 100.

Considering now the method of unloading the semi-trailer 200B from its mounted position upon the top of

the railway car 100, and again referring to Figures 17 and 18, and also to Figure 20, it is noted that the tractor 600 is backed onto the left-hand end of the railway car 100, in the manner previously explained, until the rear end of the chassis 601 thereof is located immediately forwardly with respect to the hitch 300 in its erected position supporting the front end of the semi-trailer 200B. Upon further rearward movement of the tractor 600 along the top of the railway car 100, the fifth-wheel mechanism 603 is moved below the front end of the semitrailer 200B and then the abutments 608 and 609 sequentionally engage the respective cooperating strike buttons 531 and 381. More particularly, when the abutment 603 engages the strike button 531, the fifth-wheel mechanism 500 is operated in the manner previously explained; whereby the locking jaws 518 incorporated therein are operated into their unlocking positions with respect to the king pin 202 carried by the front end of the semi-trailer 200B; when the abutment 609 engages the strike button 381, the cam 383 is operated to actuate the latch structure 304 into its unlatching position with respect to the front tie bar 406 of the shock-absorbing mechanism 400. Also, the impact from the abutment 609 carried by the rear end of the chassis 601 of the tractor 600 and the strike button 381 effects rotation of the standard 302 in the clockwise direction, with the trunnion 301, as viewed in Figure 18; whereby the hitch 300 is moved from its erected position of Figure 18 back into its storage position of Figure 17 fundamentally by the action of gravity. In the movement of the hitch 300 out of its erected position, the fifth-wheel mechanism 500 disengages the front end of the semi-trailer 200B and immediately thereafter the fifth-wheel mechanism 603 engages and supports the front end of the semi-trailer 200B effecting locking in place of the king pin 202 carried by the front end of the semi-trailer 200B. At this time, the front end of the semi-trailer 200B is supported upon the fifth-wheel mechanism 603 carried by the rear end of the chassis 601 of the tractor 600, whereby the tractor 600 may be driven forwardly off of the left-hand end of the railway car 100 drawing the coupled semi-trailer 200B along therewith, so as to complete the unloading operation. In view of the foregoing, it will be understood that the rearward movement of the tractor 600 along the top of the railway car 100 in the unloading operation described above, is continuous; whereby a flying transfer is made of the support of the front end of the semi-trailer 200B from the fifth-wheel mechanism 500 carried by the hitch 300 to the fifth-wheel mechanism 603 carried by the rear end of the chassis 601 of the tractor 600; and simultaneously the hitch 300 is moved from its erected position of Figure 18 back into its storage position of Figure 17.

Referring now to Figure 32, a modified form of the hitch 300A carried by the railway car 100 and supporting the front end of the associated semi-trailer 200B is there illustrated that is essentially of the same construction and arrangement as that previously described, except in the hitch 300A the normal upstanding attitude of the standard 302 is rearwardly inclined with respect to the vertical by an angle of about 25°. As illustrated, when the hitch 300A occupies its erected position, so that the latch structure 304 carried by the lower rear end of the strut 308 is latched to the front tie bar 406 of the shock-absorbing mechanism 400, the centre line 302 of the standard 302 is rearwardly inclined with respect to the vertical line 302" by the angle of about 25 centimeters, whereby the weight of the front end of the semi-trailer 200B acting upon the connected fifth wheel mechanism 500 tends further to rotate the standard 302 in the counterclockwise direction with the trunnion 301; which further rotation of the standard 302 is opposed by the shock-absorbing mechanism 400 through the upwardly inclined strut 308.

Accordingly, it will be understood that the shock-absorbing mechanism 400 in the hitch 300A affords cushioning for the vertical movements of the front end of the connected semi-trailer 200B, as well as to the longitudinal movements of the semi-trailer 200B relative to the centre sill 101. For example, in the event the connected semi-trailer 200B moves longitudinally toward the left with respect to the centre sill 101, this movement is transmitted through the fifth-wheel mechanism 500 to the standard 302 causing the latter to rotate with the trunnion 301 in the counterclockwise direction reducing the angle between the centre line 302' of the standard 302 and the vertical line 302", so that the standard 302 exerts a corresponding force through the strut 308 upon the shock-absorbing mechanism 400. In this movement of the semi-trailer 200B toward the left with respect to the centre sill 101, as viewed in Figure 32, the front end of the semi-trailer 200B is necessarily lifted against the action of gravity, thereby absorbing some of the energy of the moving semi-trailer 200B, the remainder of the energy of this moving semi-trailer 200B being absorbed by the shock-absorbing mechanism 400.

This arrangement is very advantageous by virtue of the particular utilization of the action of gravity in conjunction with the action of the shock absorbing mechanism 400 in cushioning longitudinal movements of the semi-trailer 200B forwardly with respect to the centre sill 101 of the railway car 100. Furthermore, the arrangement provides for cushioning of vertical movements of the front end of the semi-trailer 200B with respect to the centre sill 101 in the event the railroad bed 103 over which the railway car 100 is travelling is rough or otherwise out-of-level.

Referring now to Figures 33 to 35, inclusive, a modified form of the hitch 300B carried by the railway car 100 and supporting the front end of the associated semi-trailer 200B is there illustrated that is essentially of the same construction and arrangement as that of the hitch 300, previously described, except that in the hitch 300B, a pair of vertically disposed shock-absorbing mechanisms 700 are arranged in the extreme upper ends of the legs 305 of the standard 302 and between the lugs 312 carried at the upper ends of the legs 305 and the main body portion of the standard 302. In the arrangement, the lugs 312 are connected to the head 506 by the pivot pins 503, in the manner previously described; however, in this case, the shock-absorbing mechanisms 700 mentioned are interposed between the lugs 312 and the main body portions of the legs 305 of the standard 302, as noted above. Specifically, each of the lugs 312 is provided with a base 701 that carries a pin 702 that is arranged in sliding engagement with a bushing 703 carried by the upper end of the main body portion of the adjacent leg 305 of the standard 302; and the shock-absorbing mechanism 700 comprises a plurality of cushioning rings 704 separated by metallic washers 705, both surrounding the pin 702. Preferably, the cushioning rings 704 are formed of neoprene, or other resilient rubber-like material. Accordingly, in each shock-absorbing mechanism 700 the cushioning rings 704 and the intervening washers 705 are arranged in stacking relation between the base 701 and the bushing 703.

The fundamental operation of the hitch 300B is the same as that of the hitch 300 previously described, in that the longitudinal movements of the connected semi-trailer 200B with respect to the centre sill 101 of the railway car 100 are shocked by the main shock-absorber 400 incorporated in the centre sill 101; however, in this case, vertical movements of the front end of the connected semi-trailer 200B are shocked or cushioned by the vertical shock-absorbing mechanisms 700 incorporated directly in the standard 302, as described above.

Referring now to Figure 36, a modified form of the freight transportation system is there illustrated that comprises the railway car 100 carrying on the left-hand end thereof the unequipped road semi-trailer 200A and carrying on the right-hand end thereof a freight carrier or container 800; and preferably, the freight container 800 is of the general construction and arrangement of that disclosed in the copending application of Deodat Clejan, Serial No. 713,957, filed May 18, 1950. In the arrangement, two of the longitudinally spaced apart shock-absorbing mechanisms 400 are incorporated in the centre sill 101; and two of the semi-trailer hitches 500 are carried by the centre sill 101 and respectively operatively associated with the two shock absorbing mechanisms 400. As illustrated, the hitch 300 carried by the left-hand end of the railway car 100 occupies its erected position supporting the front end of the semi-trailer

200A, and the semi-trailer hitch 300 carried by the central portion of the railway car 100 occupies its storage position in non-interfering relation with the freight container 800 disposed thereabove and mounted upon the right-hand end of the railway car 100.

As shown in Figure 38, the freight container 800 comprises a rigid underframe 801 that carries front and rear pairs of low rollers 802 of the narrow gauge of the track rails 106 provided on the top of the centre sill 101; which low rollers 802 are flanged and face inwardly so that they are adapted to engage the track rails 106 and to straddle and to guide thereon incident to longitudinal movement of the freight container 800 in its mounted position upon the top of the centre sill 101. Accordingly, it will be understood that the freight container 800 may be loaded and unloaded in any suitable manner with respect to the top of the centre sill 101 of the railway car 100; and when the freight container 800 occupies its mounted position, it is movable longitudinally along the track rails 106 in supported position upon the low rollers 802. Further, the underframe 801 of the freight container 800 comprises elements defining a rigid hollow box-like structure 803 adjacent to the central portion thereof; which box-like structure 803 includes a pair of longitudinally extending and laterally spaced-apart latch keepers 804 depending from the bottom wall 805 of the freight container 800, as shown in Figure 39.

Further, the centre sill 101 of the railway car 100 incorporates at least on freight carrier or container hitch 900, as shown in Figures 37 and 39; which hitch 900 is adapted to cooperate with the box-like structure 803 carried by the underframe 801 of the freight container 800, when the freight container 800 occupies its mounted position upon the top of the right-hand end of the railway car 100. The freight container hitch 900 is operatively connected to the rear tie bar 405 incorporated in the shock-absorbing mechanism 400 carried by the central portion of the centre sill 101, as illustrated in Figure 37; while the semi-trailer hitch 300, not illustrated is operatively associated with the front tie bar 405 incorporated in this shock-absorbing mechanism 400, in the manner previously explained. As explained more fully hereinafter, the container hitch 900 is operative between a storage position disposed below the track rails 106 carried at the top of the centre sill 101, as illustrated in full lines in Figure 39, and an erected position disposed well above the track rails 106 and cooperating with the box like structure 803 incorporated in the underframe 801, of the freight container 800, as illustrated in broken lines in Figure 39.

Accordingly, it will be understood that when both the semi-trailer hitch 300 and the freight container hitch 900 occupy their storage positions they are disposed below the track rails 106 provided upon the top of the centre sill 101 and respectively adjacent to the front end and to the rear end of the associated shock-absorbing mechanism 400 and located in non-interfering relation with the movement longitudinally along the centre sill 101 of the road semi-trailers 200A, 200B etc. and of the freight containers 800, etc. Further, it will be appreciated that when a road semi-trailer 200A or 200B is mounted upon the right-hand end of the railway car 100, as shown in Figure 36, the semi-trailer hitch 300 is operated from its storage position into its erected position in order to support the front end of the semi-trailer and to bring about the connection of the front end of the mounted semi-trailer 200A, etc. to the shock-absorbing mechanism 400 disposed at the central portion of the railway car 100. On the other hand, when the freight container 800 is mounted upon the right-hand end of the railway car 100, as shown in Figure 36, the container hitch 900 is operated from its storage position into its erected position to connect the underframe 801 of the freight container 800 to the shock-absorbing mechanism 400 disposed at the central portion of the railway car 100. Accordingly it will be appreciated that the railway car 100, shown in Figure 36, is arranged to transport indiscriminately, unequipped road semi-trailers 200A, equipped road semi-trailers 200B, and freight containers 800.

Referring now more particularly to Figures 37 and 39, the freight container hitch 900 comprises an outer substantially rectangular box-like frame or cradle 901 that is arranged between the webs of the I-beams 104 of the centre sill 101 and provided with a pair of laterally outwardly extending supporting arms 902 that carry a pair of shoes 903 that are disposed in sliding engagements with a pair of trackways 904 arranged immediately below the inwardly directed portions of the top flanges 105 of the I-beams 104, whereby the cradle 901 is mounted for guided longitudinal sliding movements with respect to the centre sill 101 as established by the cooperation between the shoes 903 and the trackways 904. A substantially rectangular box-like plunger or piston 905 is arranged within the cradle 901 and mounted thereupon for vertical sliding movements with respect thereto, the upper end of the piston 905 being closed by a top plate 906. Arranged within the piston 905 is a jack mechanism 907 that is provided with a body 908 suitably secured to the rear tie bar 405 of the shock-absorbing mechanism 400; and which jack 907 is provided with an upstanding threaded screw 909 terminating in a head 910 engaging the undersurface of the top plate 906. The jack 907 comprises conventional mechanism for selectively projecting and retracting the screw 909, thereby selectively to elevate and to lower the head 910, with the result that the piston 905 may be selectively elevated and lowered with respect to the cradle 901. The mechanism for selectively projecting and retracting the screw 909 is arranged in the body 908 and is selectively operated by an associated rotatable operating rod 911. The lower ends of the laterally spaced apart side walls of the piston 905 are slotted, as indicated at 912, and receive the opposite ends of the rear tie bar 405 in straddling relation therewith; whereby the rear tie bar 405 and the piston 905 are secured together for longitudinal movements with respect to the centre sill 101; which longitudinal movements of the piston 905 are transmitted to the cradle 901 and guided by the shoes 903 cooperating with the trackways 904.

The operating rod 911, comprising a part of the jack mechanism 907, projects laterally through one of the slots 912 provided in the left-hand side wall of the piston 905 and thence further laterally outwardly through an elongated longitudinally extending slot 104a provided in the web of the adjacent left-hand I-beam 104, so that the operating rod 911 is moveable with the jack 907 in its movements longitudinally with the rear tie bar 405 with respect to the centre sill 101. In view of the foregoing it will be appreciated that by rotation of the operating rod 911 in one direction from the exterior of the centre sill 101, the jack mechanism 907 is operated to project the screw 909 with respect to the body 908 causing the head 910 to rise, so as to elevate the plunger 905 with respect to the cradle 901. On the other hand, when the operating rod 911 is rotated in the opposite direction from the exterior of the centre sill 101, the screw 909 of the jack mechanism 907 is retracted with respect to the body 908 causing the head 910 to be lowered, with the result that the piston 905 is lowered with respect to the associated cradle 901. Thus it will be understood that when the freight container 800 is mounted upon the top of the centre sill 101 so that the box-like structure 803 provided in the underframe 801 thereof is in vertical alignment with the piston 905 of the freight container hitch 900, the piston 905 may be selectively projected and retracted with respect to the box-like structure 803 by selective rotations of the operating shaft 911 in opposite directions. More particularly, when the operating shaft 911 is rotated in the one direction, the piston 905 is projected with respect to the cradle 901 and thus operated into its erected position, wherein it is disposed within the box-like structure 803, as indicated by the broken lines in Figure 39. On the other hand, when the operating shaft 911 is rotated in the other direction, the piston 905 is retracted with respect to the cradle 901 and thus operated into its storage position, wherein it is disposed completely out of the box-like structure 803 provided in the underframe 801.

Further, the freight container hitch 900 comprises a pair of laterally spaced-apart and inwardly directed ears 912 to which a pair of levers 913 are pivotally connected by a pair of pivot pins 914. Each of the levers 913 is substantially L-shaped and the inner end of one of the

arms thereof is pivotally connected to a downwardly projecting operating rod 915 by an associated pivot pin 916, and the outer end of the other of the arms thereof carries a latch 917 pivotally connected thereto by an associated pivot pin 918. The outer end of each of the latches 917 is arranged in a cooperating latch opening 919 arranged in the adjacent side wall of the piston 905; and each of the latches 917 is movable between a projected latching position and a retracted unlatching position. Also, each of the latches 917 is biased into its retracted unlatching position by an associated coil spring 920, one end of the coil spring 920 being connected to the inner end of the latch 917 and the other end of the spring 920 being connected to the opposite wall of the piston 905. The operating rods 915 extend downwardly in the piston 905 and project through a corresponding pair of laterally spaced-apart holes 921 provided in the rear tie bar 405 of the shock-absorbing mechanism 400; and the extreme lower ends of the operating rods 915 carry a pair of enlarged heads 922.

When the piston 905 occupies is storage position as illustrated in solid lines in Figure 29, the operating rods 915 project through the holes 921 provided in the rear tie bar 405, so that the heads 922 carried by the operating rods 915 are disposed well below the rear tie bar 405; and the coil springs 922 retain the latches 917 in their retracted or unlatching positions with respect to the latch openings 919 provided in the side walls of the piston 905. Now as the piston 905 is moved upwardly from its storage position, as shown in full lines in Figure 39, toward its elected position as shown in broken lines in Figure 39, the ears 912 move upwardly therewith carrying the latches 917 and the operating rods 915 upwardly with the piston 905. Immediately preceding the final erected position of the piston 905 in its upward movement, the enlarged heads 922 carried by the lower ends of the operating rods 915 engage the rear tie bar 405 adjacent to the holes 921 provided therein, thereby arresting further upward movement of the operating rods 915 with the piston 905. Accordingly, further upward movement of the piston 905 into its final erected position, as illustrated in dotted lines in Figure 39, causes the ears 912 to move further upwardly, so that the downward forces exerted upon the operating rods 915 by the rear tie bar 405 bring about rotation of the levers 913 in opposite directions, thereby projecting the latches 917 laterally outwardly through the associated latch openings 919 provided in the side walls of the piston 905 and thus into the hollow latch keepers 804, as indicated in broken lines in Figure 39.

Accordingly, at this time, when the piston 905 occupies its fully erected position, the piston 905 not only fits into the box-like structure 803 provided in the underframe 801 of the freight container 800, but also the latches 917 are projected laterally outwardly into latching positions with respect to the associated hollow keepers 804 forming a part of the underframe 801. Hence, the piston 905 in its fully erected position securely latches the underframe 801 thereto, whereby the longitudinal movements of the freight container 800 along the centre sill 101 are transmitted to the piston 905 effecting corresponding longitudinal movements of the cradle 901 that, in turn, is arranged in straddling relation with respect to the rear tie bar 405; whereby the longitudinal movements mentioned are transmitted to the shock-absorbing mechanism 400. Accordingly, the shock-absorbing mechanism 400 shocks, cushions and limits the longitudinal movements of the freight container 800 with respect to the centre sill 101 of the railway car 100. Moreover, the laterally projecting latches 917 in their latching positions in the latch keepers 804 prevent lateral tilting or displacement of the underframe 801 of the freight container 800 with respect to the centre sill 101.

Subsequently, when the piston 905 is returned from its fully erected position back toward its storage position, the downward movements of the ears 912 relieve the forces exerted upon the operating rods 915, so that the coil springs 920 withdraw the latches 917 from their projected latching positions back into the piston 905 and into their retracted unlatching positions with respect to the latch openings 919 provided in the side walls of the piston 905, whereby the latches 917 disengage the latch keepers 804 provided in the underframe 801 of freight container 800. When the latches 917 are thus returned back into their unlatching positions with respect to the latch keepers 804, the piston 905 may be then returned back into its fully retracted or storage position, as illustrated in solid lines in Figure 39.

By way of recapitulation, it is noted that the railway car 100, shown in Figures 1 and 2, comprises two longitudinally spaced-apart shock-absorbing mechanisms 400 incorporated in the centre sill 101 thereof and two longitudinally spaced-apart semi-trailer hitches 300 carried by the centre sill 101 thereof and respectively cooperating with the shock-absorbing mechanisms 400. The modified form of the railway car 100, as shown in Figure 36, is identical to the railway car 100 shown in Figures 1 and 2, except that it further comprises at least one freight container hitch 900 carried by the centre sill 101 thereof and cooperating with one of the shock-absorbing mechanisms 400 incorporated in the central portion of the centre sill 101; whereby this shock-absorbing mechanism 400 cooperates selectively with one of the semi-trailer hitches 300 and with the container hitch 900. Further, it will be understood that two of the freight container hitches 900 may be carried by the longitudinally spaced-apart centre sill 101 of the railway car 100 and arranged respectively to cooperate with the two shock-absorbing mechanisms 400 incorporated therein.

As a constructional example of the railway car 100; the flanged wheels carried by the trucks 102 and cooperating with the track rails 103 are of standard rail gauge; the longitudinal distance between the striker plates carried at the opposite ends of the centre sill 101 is 85 ft. 8 in.; the vertical distance between the top of the road platforms 107 carried by the centre sill 101 and the top of the truck rails 103 is 3 ft. 4in.; the vertical distance between the top of the top flanges 106 of the I-beams 104 incorporated in the centre sill 101 and the top of the road platforms 107 is 8 in.; the lateral distance between the downwardly turned flanges 109 carried by the opposite sides of the road platforms 107 is 8 ft. 4 in.; the lateral distance between the outside edges of the top flanges 106 of the I-beams 104 incorporated in the centre sill 101 is 3 ft. 3½ in. ±¼ in ; the lateral distance between the inside edges of the top flanges 106 of the I-beams 104 incorporated in the centre sill 101 is 1 ft. 5-15/16th. ±¼ in.; and the other dimensions involved are generally related to those mentioned above in accordance with the scales of the various figures of the drawings.

In view of the foregoing, it is apparent that there has been provided an improved freight transportation system involving a railway car, equipped road semi-trailers, unequipped road semi-trailers, freight containers, equipped tractors and unequipped tractors; wherein the railway car incorporates either, or both, an improved semi-trailer hitch and an improved freight container hitch, as well as a shock-absorbing arrangement operatively associated with the hitch or hitches. Also, the railway car is of the universal type in that it is capable of transporting indiscriminately equipped road semi-trailors, unequipped road semi-trailers and freight containers, while affording shock absorption protection to the transported road semi-trailer or freight container during the transportation thereof. Further, the railway car embodies an improved road wheel guiding arrangement accommodating ready loading of the road semi-trailers thereupon without damage to the rubber of the wheels of the road semi-trailer. Furthermore, there is provided a road semi-trailer hitch of improved and simplified construction and arrangement, and also a freight container hitch of improved construction and arrangement. Finally, the road semi-trailer hitch comprises a fifth wheel mechanism of improved and simplified construction and arrangement.

While there has been described what is at present considered to be the preferred embodiment of the invention, it will be understood that various modifications may be made therein, and it is intended to cover in the appended claims all such modifications as fall within the true spirit and scope of the invention.

We claim:

1. A hitch for a road semi-trailer comprising a pair of longitudinally extending and laterally spaced-apart supports, an element extending laterally between said supports and mounted at the opposite ends thereof upon said supports for rotation about its own axis, a standard rigidly secured at the lower end thereof to the intermediate portion of said element, whereby said standard is mounted for pivotal movements with said element and about the axis thereof extending transversely of said supports, said standard being selectively pivotally movable between a storage position and an erected position, said standard in its storage position being disposed between said supports and in its erected position being disposed from between said supports, a motion limiting and cushioning device carried by said supports, latching mechanism having a set position connecting said standard to said device and a trip position disconnecting said standard from said device, means responsive to pivotal movement of said standard into its erected position for setting said latching mechanism, said standard in its erected position being biased by said connected device into a normal upstanding attitude and being pivotable fore-and-aft with respect thereto longitudinally of said supports against the bias of said connected device, means operative to trip said latching mechanism, said standard being biased into its storage position, said standard being biased into its storage position, whereby said standard is pivoted into its storage position in response to tripping of said latching mechanism, and a fifth-wheel mechanism carried by the upper end of said standard and adapted to be disposed in the erected position of said standard below and in supporting relation with the front end of a cooperating semi-trailer, said fifth-wheel mechanism also being selectively operative into active and inactive positions with respect to the cooperating king pin carried by the front end of the supported semi-trailer, said fifth-wheel mechanism in its active position connecting and holding the cooperating king pin and in its inactive position disconnecting and releasing the cooperating king pin, said fifth-wheel mechanism and a connected semi-trailer being movable as a unit longitudinally of said supports effecting corresponding pivotal movements of said standard in its erected position fore-and-aft with respect to its normal upstanding attitude and longitudinally of said supports, whereby said connected device limits and cushions the movements of the connected semi-trailer longitudinally of said supports.

2. The hitch according to Claim 1, wherein a longitudinally extending trackway is carried by the supports, a strut is pivotally connected at one end thereof to the intermediate portion of the standard for pivotal movements with respect to an axis extending transversely of said supports, the other end of said strut is mounted for guided longitudinal movements along said trackway, whereby the pivotal movements of said standard are guided by said strut cooperating with said trackway, and said standard in its erected position is biased through said strut by the connected device.

3. The hitch according to Claim 1 or 2, wherein means including resilient members are arranged between the opposite ends of the laterally-extending element and the supports for mounting said element upon said supports for rotation about its own axis.

4. The hitch according to Claim 1, 2 or 3, wherein the standard is gravity biased into its storage position and counter-balancing means is arranged between the laterally-extending element and at least one of the supports opposing pivotal movement of said standard into its storage position, thereby to minimize the torque required to pivot said standard from its storage position into its erected position.

5. The hitch set forth in Claim 4, wherein said counter-balancing means essentially comprises an elastic element that is strained in response to pivotal movement of the standard into its storage position, thereby exerting a reactive torque upon said standard tending to pivot the same out of its storage position toward its erected position.

6. The hitch according to any of Claims 1 to 5, wherein the laterally-extending element is a hollow tubular element having a torsion bar arranged therein and connected at the opposite ends thereof respectively to one of the supports and to said element, said torsion bar being strained by pivotal movement of the standard into its storage position, thereby exerting a reactive torque upon said standard tending to pivot the same out of its storage position toward its erected position.

7. The hitch according to any of Claims 1 to 6, wherein the standard in its erected position is biased by the connected device into a normal upstanding attitude inclined rearwardly to the vertical and is pivotable with respect thereto against the bias of said connected device, whereby fore-and-aft movements of said standard with respect to its normal upstanding attitude and longitudinally of said frame effect corresponding up-and down movements of the upper end thereof with respect to said frame.

8. The hitch according to Claim 7, wherein the fifth-wheel mechanism and the front end of a connected semi-trailer are moveable as a unit vertically with respect to the frame effecting corresponding pivotal movements of the standard in its erected position up-and-down with respect to its normal upstanding attitude and vertically of said frame, whereby said connected device limits and cushions the movements of the connected semi-trailer vertically of said frame.

9. The hitch according to Claim 7 or 8, wherein a shock-absorbing mechanism is carried by the upper end of the standard, and the fifth-wheel mechanism is carried by said shock-absorbing mechanism and adapted to be disposed in the erected position of said standard below and in supporting relation with the front end of a co-operating semi-trailer.

10. The hitch according to any of Claims 7 to 9, wherein the fifth-wheel mechanism includes a head mounted upon the upper end of the standard for pivotal movements with respect thereto about an axis extending transversely thereof, said head in the erected position of said standard being adpated to be disposed below and in supporting relation with the front end of a cooperating semi-trailer, and locking mechanism carried by said head and selectively operative into locked and unlocked positions with respect to the cooperating king pin carried by the front end of the supported semi-trailer.

11. The hitch according to any of Claims 7 to 10, wherein a pair of outwardly projecting and laterally spaced apart lugs are carried by the upper end of the standard, means including a pair of laterally spaced-apart and axially aligned pins connect the head to said lugs for pivotal movements with respect to said standard about an axis extending transversely thereof, and means including a pair of laterally spaced-apart resilient elements act between said standard and said head to bias said head into a normal attitude disposed substantially normal to the axis of said standard in its erected position.

12. The hitch according to any of the preceding claims, combined with a railway car, said railway car including a longitudinally extending frame comprising said supports and a pair of trucks supporting the opposite ends of said frame, said frame being adapted to support a trailer mounted upon the top thereof, said standard being mounted upon said frame for pivotal movements with respect thereto about an axis extending transversely thereof, said standard in said storage position disposed being closely adjacent to the top of said frame and in said erected position disposed well above the top thereof.

13. The railway car combination according to Claim 12, wherein the frame includes a longitudinally extending hollow center sill, the pair of trucks support the opposite ends of said center sill, said center sill being adapted to support a trailer mounted upon the top thereof, the standard is mounted upon said center sill for pivotal movements with respect thereto about an axis extending transversely thereof, said standard being selectively pivotally movable between a storage position disposed within said hollow center sill and below the top thereof and an erected position disposed out of said hollow center sill and above the top thereof, and the motion limiting and cushioning device is carried by said center sill.

14. The railway car combination according to Claims 12 and 13 wherein said fifth wheel mechanism carried by the upper end of the standard and a connected trailer mounted upon the top of said center sill are movable as a unit longitudinally of said center sill effecting corresponding pivotal movements of said standard in its erected position fore-and-aft with respect to its normal upstanding attitude and longitudinally of said center sill, whereby the connected device limits and cushions the movements of the mounted trailer longitudinally of said center sill.

15. The railway car combination according to Claim 12 13 or 14, including a longitudinally extending trackway carried by said frame for guiding the pivotal movements of said standard.

16. The railway car combination according to Claim 15, including a strut for selectively pivotally moving the standard, means mounting one end of said strut upon the intermediate portion of said standard for pivotal movements with respect thereto about an axis extending transversely of the frame, and means mounting the other end of said strut for guided longitudinal movements along the trackway, whereby the pivotal movement of said standard are guided by said strut cooperating with said trackway.

17. The railway car combination according to any of Claims 12 to 16, wherein the standard is gravity biased into its storage position and counter-balancing means oppose pivotal movement of said standard into its storage position, thereby to minimize the torque required to pivot said standard from its storage position into its erected position.

18. The railway car combination according to any of Claims 12 to 17, including a pair of longitudinally extending and laterally spaced-apart platforms carried by the frame respectively adjacent to the opposite sides thereof and constituting a roadway of the standard road gauge whereby said roadway is arranged to engage and to support the road wheels of a semi-trailer so as to mount the same upon the top of said frame for longitudinal movements thereslong, and a pair of longitudinally extending and laterally spaced-apart wheel guides carried by said frame and respectively disposed on opposite sides of the centerline thereof, each one of said wheel guides being disposed adjacent to the inside edge of the adjacent one of said platforms and projecting upwardly therefrom, the lateral distance between each one of said wheel guides and the outer edge of the opposite one of said platforms being somewhat greater than the standard road gauge of the rear wheels of a semi-trailer mounted upon the top of said body, thereby positively to prevent lateral displacement of the mounted semi-trailer from the top of said frame, each one of said wheel guides also being provided with a smooth outwardly facing rubbing surface adapted to engage the adjacent inside surface of the associated one road wheel of a semi-trailer mounted upon the top of said body incident to longitudinal movement thereof along said body in the event of substantial misalignment between the centerline of said frame and the centerline of the mounted semi-trailer, whereby said one wheel guide exerts a reactive force laterally outwardly upon the engaged inside surface of the one road wheel tending to rotate the rear end of the mounted semi-trailer in order to minimize the misalignment aforesaid thus to effect centering of the mounted semi-trailer with respect to said frame.

19. The railway car combination according to Claim 18, wherein each of the wheel guides consists essentially of an elongated tubular structure extending substantially from end to end of the frame.

20. The railway car combination according to Claim 18 or 19, wherein the vertical distance between the top of said frame and said roadway being less than the vertical distance between the underportion of the semi-trailer and the bottoms of the road wheels carried thereby, whereby said roadway engages and supports the road wheels of a semi-trailer so as to mount the same upon the top of said frame and in straddling relation therewith and with the underportion of the semi-trailer positioned above the top of said frame and out of contact therewith.

21. The railway car combination according to Claim 20, wherein the pair of longitudinally extending and laterally spaced-apart wheel guides is respectively carried by the inner edges of the platforms.

22 The railway car combination according to Claim 18, wherein each of the platforms includes a metal sheet having an upwardly directed inner ledge, and said wheel guides comprise a pair of longitudinally extending tubular structures respectively carried by said ledges.

23. The railway car combination according to Claim 18, wherein the box like frame comprises a longitudinally extending narrow hollow center sill including a pair of longitudinally extending and laterally spaced-apart I-beams and the position of each of the wheel guides positively prevents engagement of the inside surface of the adjacent road wheel carried by the mounted semi-trailer with the top flange carried by the adjacent I-beam of said center sill so as to prevent damage to the adjacent road wheel.

24. The hitch according to any of Claims 1 to 11, combined with a railway car for transporting a road semi-trailer of the type including a rear end carrying both road wheels of standard road gauge and track rollers of given narrow gauge depending therefrom and disposed inwardly of and above the road wheels carried thereby and a front end carrying a king pin, said railway car including a longitudinally extending hollow center sill comprising said supports and a pair of trucks supporting the opposite ends of said center sill, a pair of longitudinally extending and laterally spaced-apart rails provided on the top of said center sill and constituting a track of said given narrow gauge, said track being arranged to engage and to support the track rollers carried by the trailer so as to mount the same upon the top of said center sill in straddling relation therewith and with the road wheels of the trailer projecting laterally outwardly from the opposite sides of said center sill, said standard being mounted upon said center sill for pivotal movements with respect thereto about an axis extending transversely thereof, said standard in said storage position being disposed within said hollow center sill and below the top thereof and in said erected position disposed out of said hollow center sill and above the top thereof.

25. The hitch according to any of Claims 1 to 11, wherein said fifh-wheel mechanism comprises a head including hollow substantially box-like structure provided with an open front end and vertically spaced-apart top and bottom plates, said bottom plate being adapted to engage and to support the extreme lower end of a cooperating king pin, said top plate having a guide slot therein provided with an open front and rearwardly converging side walls to define a home position for the cooperating king pin supported by said bottom plate, a pair of locking jaws arranged within said hollow head and between said plates and disposed in laterally spaced-apart relation and located on opposite sides of said guide slot, means mounting said locking jaws for pivotal movements about a pair of laterally spaced-apart upstanding axes between locking and unlocking positions with respect to a cooperating king pin in its home position, and means for selectively restraining said locking jaws in their locking positions.

26. The hitch according to Claim 25, wherein a pair of locking members is arranged within the hollow head and between the plates and disposed in laterally spaced-apart relation and located on opposite sides of said guide slot, a pair of laterally spaced-apart upstanding pivot pins is extended between said plates and respectively mounts said locking members for pivotal movements about the intermediate portions thereof, the front ends of said locking members respectively providing a pair of locking jaws movable between locking and unlocking positions with respect to a cooperating king pin in its home position, and restraining means are provided with cooperating with the rear ends of said locking members selectively to restrain said locking jaws in their locking positions.

27. The hitch according to Claims 25 and 26, wherein the hollow head includes a block arranged therewithin and mounted upon the bottom plate for longitudinal

movements between forward and rearward positions with respect to the rear ends of the locking members, said block in its forward position being positioned between the rear ends of said locking members restraining the locking jaws into their locking position, said block in its rearward position being positioned from between the rear ends of said locking members accommodating movement of said locking jaws into their unlocking position, and means for selectively moving said block between its forward and rearward positions

28. The hitch according to Claim 27, wherein the means for moving the block include means biasing said block into its forward position and an element selectively operative to move said block against said bias into its rearward position.

29. The hitch according to Claim 27, wherein the pair of locking jaws are moved with respect to the king pin in its home position by means including an elongated slide bar carried by the head and cooperating with the rear ends of the locking members for selectively moving said locking members so as selectively to operate said locking jaws between their locking and unlocking positions, said slide bar being disposed exteriorly of said hollow head and projecting forwardly of the front end thereof so that it is readily accessible from the exterior when the front end of a semi-trailer is supported by said head.

30. A freight transportation system comprising a railway car including a longitudinally extending frame supported at the opposite ends thereof by a pair of trucks, a road semi-trailer including a rear end carrying road wheels and a front end carrying a king pin, a tractor carrying road wheels, a first fifth-wheel mechanism carried by the rear end of said tractor and adapted to support the front end of said trailer and selectively to couple and to uncouple said king pin, structure carried by said frame for supporting both said trailer and said tractor mounted upon the top thereof with said first fifth-wheel mechanism coupling said king pin, thereby to accommodate movements of said mounted tractor and said coupled mounted trailer longitudinally of said frame under the motive power of said mounted tractor, a standard mounted upon said frame for pivotal movements with respect thereto about an axis extending transversely thereof, said standard being selectively pivotally movable between a substantially horizontal storage position disposed closely adjacent to the top of said frame and a substantially vertical erected position disposed well above the top of said frame, latching mechanism for connecting said standard in its erected position to said frame, said latching mechanism being automatically set to latch said standard in its erected position in response to movement of said standard from its storage position into its erected position, a second fifth-wheel mechanism carried by the upper end of said standard and movable therewith and adapted to be disposed in the erected position of said standard below and in supporting relation with the front end of said mounted trailer and also adapted automatically to couple said king pin in response to engagement thereof with said king pin, means carried by said tractor for operating said first fifth-wheel mechanism to uncouple said king pin, and additional means carried by the rear end of said tractor for pivotally moving said standard from its storage position into its erected position under the motive power of said tractor and immediately following operation of said first fifth-wheel mechanism to uncouple said king pin, whereby said first fifth-wheel mechanism may be operated from said mounted tractor to uncouple said king pin and said second fifth-wheel mechanism may be moved with said standard by said mounted tractor immediately thereafter to engage said king pin so as to couple the same, thereby to effect a flying transfer of the support of the front end of said mounted trailer from said first fifth-wheel mechanism to said second fifth-wheel mechanism.

31. The system of Claim 30, wherein the latching mechanism connects the standard in its erected position to a shock-absorbing device carried by the frame said standard in its erected position being biased by said compressed shock-absorbing device into a normal upstanding attitude and being pivotal fore-and-aft with respect thereto and longitudinally of said frame against the bias of said connected shock-absorbing device.

32. The system of Claim 30 or 31, wherein the flying transfer is effected in loading the semi-trailer on the railway car by placing the first fifth-wheel mechanism in its supporting position below the front end of said trailer and coupling the king pin, moving the tractor and said coupled trailer as a unit longitudinally onto the frame of said railway car and under the motive power of said tractor, connecting the rear end of said tractor to the standard when said standard is in its storage position, moving said tractor forwardly along said frame in order to pivot said connected standard from its storage position substantially into its erected position so as to position the second fifth-wheel mechanism below the front end of said trailer and adjacent to the rear end of said tractor and located behind said king pin, operating said first fifth-wheel mechanism to uncouple said king pin, then moving said tractor further forwardly along said frame in order to pivot said connected standard into its fully erected position and simultaneously to move said first fifth-wheel mechanism from its supporting position below the front end of said trailer while moving said second fifth wheel mechanism into its supporting position below the front end of said trailer and engaging said king pin to couple the same, and then disconnecting the rear end of said tractor from said standard when said standard is in its fully erected position.

33 The system according to Claim 30, including means carried by the rear end of the tractor for operating the second fifth-wheel mechanism to uncouple the king pin when said second fifth-wheel mechanism is in its supporting position with respect to the front end of the mounted trailer with the standard in its erected position, and additional means carried by the rear end of the tractor for tripping the latching mechanism with said standard in its erected position, whereby said second fifth wheel mechanism may be operated to uncouple said king pin and said latching mechanism may be tripped immediately thereafter causing said standard to pivot from its erected position back into its storage position and said first fifth-wheel mechanism may be moved with said mounted tractor immediately thereafter below and in supporting relation with the front end of said mounted trailer and to engage said king pin so as to couple the same, thereby to effect a flying transfer of the support of the front end of said mounted trailer for said second fifth-wheel mechanism to said first fifth-wheel mechanism.

34. The system of Claim 33, wherein the flying transfer is effected in unloading the semi-trailer from its mounted position upon the top of the railway car when the front end thereof is supported by the second fifth-wheel mechanism coupling the king pin with the standard in its erected position by moving the tractor in its mounted position upon the top of the frame rearwardly therealong under the motive power of said mounted tractor and to a position disposed immediately forwardly of said second fifth wheel mechanism, operating said second fifth-wheel mechanism from said rearwardly moving mounted tractor to uncouple said king pin, then tripping said latching mechanism from said rearwardly moving mounted tractor causing said standard to pivot from its erected position back into its storage position, and immediately moving the first fifth-wheel mechanism below and in supporting position with the front end of said trailer causing said first fifth-wheel mechanism to engage said king pin so as to couple the same.

35. A hitch for a road semi-trailer substantially as herein described with particular reference to the drawings.

36. A railway car substantially as herein described with particular reference to the drawings.

37. A freight transportation system substantially as herein described.

R. HALL
of REMFRY & SON
Agent for the Applicants.

Dated this 21th day of December 1960.

M.o.I.P.C.—L.—109 Patent/62—19-6-63—100.

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74665, filed 24th December 1960/3rd Paus 1882 (Saka). Reciprocity dated (United Kingdom)—30th December 1959. (Accepted 6th April 1962.)

PLASTIC COMPOSITIONS AND PRODUCTS THEREOF.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, MANUFACTURERS, OF IMPERIAL CHEMICAL HOUSE, MILLBANK, LONDON, S.W.1., ENGLAND, A BRITISH COMPANY.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to compositions comprising polythene, the normally solid polymers of ethylene, and to products thereof.

It has previously been proposed to add to polythene carbon black and other inert fillers, for example finely divided calcium carbonate, to improve certain mechanical properties, particularly to increase the hardness and tensile strength and raise the softening point. The average particle size of carbon blacks hitherto used for this purpose has been upwards of 50 milli-microns, while it has been proposed to use finely divided calcium carbonate of particle size less than 1 micron, with at least 50% less than 0.1 micron.

Amounts of carbon black up to about 4% by weight of the polythene have been used to pigment the polythene and protect it against ultra-violet light, and such quantities can be tolerated without affecting the mechanical properties; but it has been found that when larger amounts of such fillers are added the improvement obtained in tensile strength is accompanied by a lowering of the flexibility and an increase in brittleness of the polythene

We have now found that by using carbon black or other inert fillers of extremely small particle size, not only may the tensile strength of the polythene be improved without significant impairment of the flexibility or rise in brittleness but the flow properties of the polythene, and hence the processability, may be substantially improved. We have found moreover that both the tensile strength and the processability of the polythene are improved by much smaller quantities of the carbon black or other filler than are required to effect the same degree of improvement by the addition of fillers of coarser particle size.

In accordance with the present invention, an improved polythene composition comprises polythene and from 5 to 25 parts per 100 parts of polythene, by weight, of an inert filler having an average particle size not exceeding 150 Å.

In accordance with a further feature of the invention, a process for the production of shaped structures comprises shaping at a temperature above its softening temperature a composition comprising polythene and from 5 to 25 parts per 100 parts of polythene, by weight, of an inert filler having an average particle size not exceeding 150 Å.

The average particle size of the filler preferably does not exceed 50 Å. Suitable fillers include, for example: carbon black; inorganic carbonates such as calcium and magnesium carbonates; silica; silicates such as calcium, sodium-aluminium, potassium, aluminium, sodium and magnesium silicates; coated silicates such as those sold under the Registered Trade Marks "Winnofil" and "Aerosil" FK3 and sulphates such as barium sulphate.

The fillers may be incorporated with the polythene by any of the conventional methods, for example by milling on open rolls or in a Banbury mill or other high shear mixer.

The most significant improvement obtained in the compositions of this invention compared with unmodified polythene is the improvement in flow properties, indicated by the absence of turbulence in the composition when extruded at high rates of shear. Therefore, the compositions are of particular value for the production of shaped structures by extrusion or by injection moulding or extrusion moulding. Such processes may be operated at much higher rates with these compositions than with the unmodified polythene. We have found, moreover, that such improved flow rates can be obtained by the addition of fillers of coarser particle size only if these are added in quantities much larger than are needed of the fillers used in the compositions of these invention.

The substantial improvement in properties of the compositions of these invention compared with filled compositions of the prior art and with the unmodified polythene is illustrated by the following Examples, in which all parts given are by weight.

Example 1 and 2.

Samples of polythene produced by a high pressure process and having a melt flow index of 4 were mixed with varying amounts of carbon black or silica filler, by milling the polythene with the filler on open rolls at 130°C. until complete dispersion was obtained. Samples milled with fillers of very small particle size, in accordance with this invention, were compared with samples similarly prepared but containing fillers of coarser particle size. The various samples were tested by means of a ram extruder, and the concentration of each filler that was required to give an extrudate free from turbulence at a shear rate of 196 secs.$^{-1}$ was determined for each filler. The physical properties of the extruded composition were also noted. The findings are summarised in the following table.

Filler	Particle size of filler Å	Minimum Conc. required to give a turbulent free extrudate at a shear rate 196 sec.$^{-1}$ (Parts/100 parts polythene)	Melt Viscosity 10⁴ poises	Physical Properties		
				Break Strength at 20°C p. s. i.	Yield Strength at 20°C p. s. i.	% Elongation at Break 20°C
None	—	(Turbulent at 50 sec.$^{-1}$)	3.4	2230	1670	338
Carbon black Kosmotherm 'M'	4,700 (average)	100 parts	5.0	2430	2430	16
Carbon black Kosmovar	36 (average)	15 parts	3.5	2120	1840	329
Kieselguhr	20,000 (average)	100 parts	10.0	2360	2360	11
Hydrated silica Aerosil 2491/380	30-150 (range)	15 parts	3.4	1850	2030	113

The physical properties were measured on dumbbell specimens using a Hounsfield Rubber Tensometer with modified recording and measuring equipment (ring dynometer with Sunvic Chart recorder). The dumbbells were pulled on this tester at 20 inches per minute.

We claim :

1. A composition comprising polythene and from 5 to 25 parts per 100 parts of polythene, by weight, of an inert filler having an average particle size not exceeding 150 Å.

2. A composition as claimed in Claim 1 in which the average particle size of the filler does not exceed 50 Å.

3. A composition as claimed in Claim 1 or Claim 2 in which the inert filler is carbon black.

4. A composition as claimed in Claim 1 or Claim 2 in in which the inert filler is silica.

5. A process for the production of articles comprising polythene that consists in shaping at a temperature above its softening temperature a composition comprising polythene and from 5 to 25 parts per 100 parts of polythene, by weight, of an inert filler having an average particle size not exceeding 150 Å.

6. A process as claimed in Claim 5 in which the average particle size of the filler does not exceed 50 Å .

7. A process as claimed in Claim 5 or Claim 6 in which the inert filler is carbon black.

8. A process as claimed in Claim 5 or Claim 6 in which the inert filler is silica.

9. A process as claimed in any of Claims 5 to 8 in which the composition is shaped by extrusion.

10. A process as claimed in any of Claims 5 to 8 in which the composition is shaped by extrusion moulding or injection moulding.

11. Articles comprising polythene whenever produced by a process as claimed in any of Claims 5 to 10.

R. HALL.

or REMFRY & SON.

Agent for the Applicants.

Dated this 24th day of December 1960.

MGIP Santh.—SL—34 Patent/62—18-1-63—100.

INSPECTION CENTRE

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74665, filed 24th December 1960, 3rd Pausa 1882 (Saka). Reciprocity date (United Kingdom)—1st January 1960. (Accepted 26th May 1961.)

COPPER ARTICLES COATED WITH POLYMERIC COATINGS.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, MANUFACTURERS, OF IMPERIAL CHEMICAL HOUSE, MILLBANK, LONDON, S. W. 1, ENGLAND, A BRITISH COMPANY.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to copper articles coated with polymeric coatings.

It is well known that it is desirable to incorporate antioxidants into rubber and polymers and copolymers of aliphatic unsaturated hydrocarbons, *e.g.*, polythene (the solid polymers of ethylene), polypropylene, polyisobutylene and the polymers and copolymers of butadiene and isoprene. These materials have good insulating properties and are therefore desirable for use as insulating coatings on copper.

The solid polymers of propylene, particularly isotactic polypropylene by which we mean a solid polypropylene not less than 75 per cent. of which is insoluble in heptane, are materials with excellent mechanical and electrical properties which are easily shaped into strips, ribbons and coatings by normal shaping processes of the plastics industry such as extrusion. It has generally been found, however, that these polymers are rapidly degraded and become brittle when in the presence of copper, particularly when they are subjected to elevated temperatures and/or ultra violet light, even when they have admixed with them the best antioxidants known in the art.

The object of the present invention is to provide insulated copper articles, *e.g.*, coated wire, mouldings with copper inserts and condensers, in which the insulant composition comprises a polymer of propylene with a valuable stability to oxidative degradation even at elevated temperatures.

According to the present invention we provide articles comprising copper and a polymeric composition in close contact therewith, said polymeric composition comprising a solid polymer of propylene and as stabiliser therefor N,N′-di-β-naphthyl p-phenylene diamine.

The content of the di-β-naphthyl-p-phenylene diamine in these compositions may be varied over wide limits. It is usually sufficient to use from 0.05 to 5 per cent. of the said di-β-naphthyl-p-phenylene diamine by weight of the composition, and in general 0.2 to 1 per cent. of the said di-β-naphthyl-p-phenylene diamine by weight of the composition is sufficient.

This compositions of this invention may be made by any of the mastication processes. A satisfactory method for mixing the stabilising ingredient with isotactic polypropylene made by the low pressure process is to add a solution of the stabilising ingredient to isotactic polypropylene powder obtained by this process and then to remove the solvent for the stabilising component by evaporation.

The compositions of this invention may also contain other stabilisers such as materials which absorb ultra violet light. They may also contain further ancillary ingredients such as processing aids, for example, the soaps of calcium and zinc, and also such materials as pigments, dyes and fillers. Thus, carbon black may be incorporated either as an absorber of ultra violet light or as a pigment.

The following experimental details illustrate our invention. It will be understood, however, that our invention is in no way limited by these details.

Polypropylene of melt flow index 5 (as measured by the A.S.T.M. method modified by using a 10 kg. weight instead of the weight specified for causing extrusion) was mixed on open rolls at 165°C. with respectively 1 per cent. by weight of di-β-naphthyl-p-phenylene diamine and 0.5 per cent. by weight of a condensate of p-nonyl phenol with acetone in conjunction with 0.5 per cent. by weight of dilauryl thiodipropionate as set out in the following Table.

Samples were pressed on to copper sheet of thickness .005" to give a coating of thickness .020".

Further samples were extruded on to copper wire of diameter .036" to give a coating of thickness .016".

These coated sheets and wires were held in an air oven at 140°C. until the coatings were found to be brittle when handled.

Comparative tests were performed on thin sheets about .020" thick prepared from the compositions by moulding at 190°C. and on copper sheets and wires coated with the compositions.

The results of the tests were as follows.

Expt	Sample	Period until brittle (hrs.)		
		On wire	On foil	No Cu Present
1	No additive	< 25	< 25	[illegible]
2	1 % di-β-naphthyl-p-phenylene diamine	325	930	> 1,0[illegible]
3	0·5% p-nonylphenol/acetone condensate + 0·5% dilauryl thiodipropionate	< 25	< 25	680

We claim:

1. Articles comprising copper and a polymeric composition in close contact therewith, said polymeric composition comprising a solid polymer of propylene and as stabiliser therefor N,N′-di-β-naphthyl p-phenylene diamine.

2. Articles according to Claim 1 in which the solid polymer of propylene is isotactic polypropylene.

3. Articles according to either of the preceding claims in which the quantity of stabiliser used is from 0.05 to 5 per cent. by weight of the composition.

4. Articles according to Claim 3 in which the quantity of stabiliser used is from 0.2 to 1 per cent. by weight of the composition.

5. Articles substantially as hereinbefore described, with particular reference to Experiment 2.

R. HALL,

of REMFRY & SON,

Agent for the Applicants.

Dated this 24th day of December 1960.

Price: TWO RUPEES.

MGIPC—L—104 Patent/62—25-5-63—100.

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74668, filed 24th December 1960./3 Paus 1882 (Saka).

(Accepted 12th February 1962.)

" PROCESS FOR THE PREPARATION OF AN IMPROVED DRYING OIL FROM CASTOR OIL. "

THE TATA OIL MILLS COMPANY LIMITED, A PUBLIC LIMITED COMPANY INCORPORATED IN INDIA, OF BOMBAY HOUSE, BRUCE STREET, FORT, BOMBAY 1, BOMBAY, INDIA.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This invention relates to the preparation of an improved drying oil from castor oil.

Castor oil contains a large percentage of ricinoleic acid present in combination as glycerides. Dehydration of castor oil results in the liberation of water and conversion of ricinoleic acid glycerides to glycerides of 9, 12-linoleic acid and 9, 11-linoletic acid having good drying properties. Rassow (Angew. Chem. 26, 316, 1913) observed that dehydration of castor oil can be effected by heating it in the presence of acid catalysts like sulphuric acid. It has been observed later that the dehydration of castor oil can be brought about by a number of other catalysts under different conditions of temperature, pressure, concentration of catalyst and period of reaction.

Dehydrated castor oil has got a unique combination of desirable properties like high water resistance and non-yellowing nature but it has got the undesirable property of "after-tack" in air dried films which persists for a long time. This defect is carried over to oleoresinous and oil modified alkyd varnishes made from it.

The object of our invention is to provide a process for the preparation of an improved drying oil from castor oil which will be free from the defect of after tack.

We have now found, according to our invention, that if castor oil is subjected to an initial partial thermal decomposition treatment in the absence of any dehydrating catalyst and then the residual oil obtained is subjected to a dehydration treatment in the presence of a dehydration catalyst, a drysng oil results which is free from the defect of "after tack". This initial heat treatment in the absence of a dehydration catalyst is one of the essential features of our invention.

The following examples are given in order to describe the process clearly but do not, however, limit the scope of the invention.

Example 1

100 lbs of castor oil are taken in a stainless steel distillation vessel provided with a stirrer, condenser, receiver and connections to a vacuum pump. The vessel is provided with cooling coils and arrangement for heating the oil.

The oil is heated to 270°C-285°C under a vacuum of 10-29 inches of mercury when thermal decomposition of the oil sets in. The temperature is gradually raised to 320°-340°C and maintained till about 68-70 lbs of residual oil are left in the distillation vessel and 29-30 lbs of distillate are collected in the receiver. The residual oil is then quickly cooled down to 30°-50°C under vacuum by passing water through the cooling coils. Then the dehydration catalyst which consists of 0.2 lbs of concentrated sulphuric acid is added to the residual oil in the distillation vessel. The temperature of the oil is then raised slowly to 250°-340°C under a vacuum of 10-29 inches of mercury. The undecomposed glycerides of ricinoleic acid in the oil undergo dehydration and water distills out. The temparature of the oil is maintained till no more water distills out. The water usually evolved amounts to 1-2% on the weight of castor oil taken. Then the oil is cooled down to room temperature and used as a drying oil.

Example 2

1000 lbs of Castor oil are taken in a distillation equipment as described under example 1. The oil is heated under vacuum of 10.29 inches of mercury and held at a temperature of 270°-285°C without increasing the temperature further. The thermal decomposition of the oil takes place at a slower rate than in the method described under example 1. The heating is continued till about 2 lbs. of distillate are collected in the receiver and 98 lbs. of residual oil are left in the distillation vessel. The oil is then cooled down to 30°-50°C and then the dehydration catalyst which cossists of 0.2 lbs of sulphuric acid is added to the oil. The temperature of the oil is now raised to 250°-340°C under a vacuum of 10-29 inches of mercury and maintained till no more water collects in the receiver. The quantity of water collected is generally about 3-4 lbs. The oil is then cooled down to room temperature and used as a drying oil.

For carrying out the dehydration treatment as above described, the preferred catalyst is sulphuric acid. A number of other catalysts like phosphoric acid, ethyl sulphate or sodium bisulphate have been found to be useful in carrying out the dehydration at a concentration of 0.1-2% based on the weight of the original castor oil taken. For convenience in addition, these catalysts, including sulphuric acid, can be mixed with five times their weight of vegetable oils like castor, linseed, tung, groundnut, modified vegetable oils like dehydrated castor oil, stand oils, oily residue obtained by cracking of vegetable oils like castor, or marine oils and the mixture used as a dehydrating agent.

The dehydration treatment can be carried out also at atmospheric pressure. A stream of an inert gas like carbon dioxide bubbled through the oil prevents oxidation changes in the oil.

The distillate obtained during the initial thermal decomposition treatment of castor oil consists of a mixture of heptaldehyde, undecylenic acid and fatty acids. These are worked up separately.

The drying oil obtained by the process described in example 1 or 2 may be mixed up with 'driers' like cobalt naphthenate, lead naphthenate as in the case of other drying oils like linseed oil and used for the manufacture of paints, varnishes, linoleum and the like.

WE CLAIM :—

1. A process for the preparation of an improved drying oil from castor oil, which comprises subjecting castor oil to an initial partial thermal decomposition treatment in the absence of any dehydrating catalyst and then subjecting the residual oil obtained to a subsequent dehydration treatment in the presence of a dehydration catalyst.

2. A process for the preparation of an improved drying oil from castor oil as in claim 1, where the oil is heated to a temperature of 270°-340°C during the initial partial thermal decomposition treatment in the absence of any dehydration catalyst.

3. A process for the preparation of an improved drying

Price : TWO RUPEES.

oil from castor oil as in claim 2, where the oil is heated to a temperature of 270°-340°C during the initial partial thermal decomposition treatment in the absence of any dehydration catalyst under vacuum of 10-29 inches of mercury.

4. A process for the preparation of an improved drying oil from castor oil as in the preceeding claims, where the castor oil is subjected to thermal decomposition treatment till for every 100 lbs of original oil taken about 68 lbs to 98 lbs of residual oil are left over for subsequent dehydration treatment.

5. A process for the preparation of an improved drying oil from castor oil as in any one of the preceeding claims where the residual of oil left over after the initial partial thermal decomposition treatment is subjected to a dehydration treatment in the presence of a dehyration catalyst.

6. A process for the preparation of an improved drying oil from castor oil as set forth in claim 5, where the dehydration catalyst employed is concentrated sulphuric acid.

7. A process for the preparation of an improved drying oil as in claim 6 where the quantity of concentrated sulphuric acid used is 0.2% on the weight of original castor oil taken.

8. A process for the preparation of an improved drying oil as in claim 5, where the dehydration treatment is carried out by raising the temperature of the oil after addition of catalyst to 250°-340°C maintaining the temperature at 250°-340°C till no more water collects as distillate and then cooling down the oil to atmospheric temperature.

9. A process for the preparation of an improved drying oil as in claim 5 where, the dehydration treatment is carried out by raising the temperature of the oil after addition of catalyst to 250°-340°C under vacuum of 10-29 inches of mercury, maintaining the temperature at 250-340°C till no more water collects as a distillate and then cooling down the oil to atmospheric temperature.

10. A process for the preparation of an improved drying oil from castor oil as claimed in claim 5 where the dehydration catalyst employed may be phosphoric acid. ethyl sulphate or sodium bisulphate at a concentration of 0.1-2% based on the weight of the original castor oil taken.

11. A process for the preparation of an improved drying oil from castor oil as claimed in claims 5 to 10 where, for convenience in addition, the catalysts may be mixed with five times their weightof vegetable oils like castor, linseed, tung or groundnut oil, or modiffied vegetable oils like dehydrated castor or stand oil, or oily residue obtained by cracking vegetable oils like castor or marine oil.

12. A process for the preparation of an improved drying oil from castor oil as claimed in the preceding claims in which the dehydration treatment may be carried out at atmospheric pressure.

13. A process for the preparation of an improved drying oil from castor oil as claimed in the preceding claims in which a stream of an inert gas like carbon dioxide may be bubbled through the oil to prevent oxidation changes in the oil.

14. A drying oil whenever prepared prepared by the process substantially as described and claimed in any of the preceding claims.

15. A drying oil as claimed in claim 14 mixed with driers liTe cobalt naphthenate or lead nephthenate for the manufacture of paints, varnishes, linoleum and the like:

R. HALL
of REMFRY & SON,
Agent for the Applicants.

Dated this 24th day of December 1960.

Printed by The Nelys Printing Works, Calcutta-1.

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17

Specification No. 74669, filed 24th December 1960./3 Paus 1882 (Saka). Reciprocity date (United Kingdom) 2nd January 1960. (Accepted 13th February 1962.)

"REVOLUTION-COUNTING MECHANISMS."

FERRANTI, LIMITED, A COMPANY REGISTERED UNDER THE LAWS OF GREAT BRITAIN, OF HOLLINWOOD, IN THE COUNTY OF LANCASHIRE, ENGLAND.

The following Specification particularly describes and ascertains the nature of this Invention and the manner in which it is to be performed :—

THIS INVENTION relates to revolution-counting mechanisms of the kind by which the count is displayed indigital form on a train of indicating wheels, such as drums or discs, carrying figures on their curved or plain surfaces, each wheel being concealed behind a panel having a window in the form of an aperture or a transparency to allow only one figure on the wheel to be seen at one time. The train is driven by a driving shaft and in effect counts the revolutions of the shaft. The displayed figures may indicate in decade form the number of revolutions made by the shaft, or may be calibrated to indicate some quantity dependent on those revolutions. For example, where the driving shaft is itself driven from the disc of an electricity meter the wheels may be calibrated to indicate direct in pounds, shillings, and pence the cost of the energy expended. For convenience of description it will however be assumed that the count is displayed in decade form.

Where the mechanism is the registering mechanism of an electricity meter, it is known to operate such a train from the driving shaft so that in each of the indicating wheels except the first—by which is meant the wheel of lowest numerical significance—the change of figure resulting from the change from 9 to 0 of the next lower wheel occurs abruptly, thereby providing a digital form display. Where it is essential to minimise the load imposed by the train on the meter, difficulties have been experience in operating the first wheel accurately so that each change of figure occurs abruptly on this wheel as well. It is however known to provide a mechanism whereby mechanical energy is stored by the shaft whilst the first wheel rotates more or less continuously between the figures 1 to 9, this energy being then suddenly released to step the wheel abruptly from 9 to 0, thereby stepping at least the next higher wheel forward by one figure as already explained. A disadvantage of this arrangement is that in order to supply the abrupt change from 9 to 0 the rotation of the wheel between 2 and 8 necessarily involves a certain amount of lost motion, to the extent of not more than one digit interval, so that the reading of the first decade over this range is in part erroneous. As the error is never greater than one digit it can be tolerated by the subscriber. For the purpose of a testing engineer, visiting the meter on site, however, an accurate indication of the first decade is necessary and it is not desirable for him to have to unseal the meter in order to see such an indication.

An object of the present invention is accordingly to provide a revolution-counting mechanism of the kind set forth which facilitates the making of an accurate reading without being likely to confuse a person making reading of the digital display of the mechanism.

In accordane with the present invention, a revolution counting mechanism includes a main train of digital indicating wheels arranged to be driven by a driving shaft through a coupling to the first indicating wheel of the train—that is the wheel of least numerical significance—, the coupling being such that said first wheel has an inaccurate response to the shaft rotation during a part at least of each complete revolution of the shaft, and supplementary display means for providing an analogue indication which is always an accurate response to the shaft rotation, such analogue indication being visible to an observer stationed to view the display of the main train but being inconspicuous compared with that display.

In the accompanying drawings,

Figure 1 shows partly in simplified elevation and in part schematically the revolution-counting mechanism of an electricity meter in accordance with one embodiment of the invention, with the dial plate of the meter removed,

Figure 2 repeats the elevational view of Figure 1 but with the plate in place,

Figures 3 and 5 correspond to Figure 1 and 2 respectively but in accordance with another embodiment,

and Figure 4 is a side view in the direction of the arrows 4,4, of a part of the mechanism of Figure 3.

In carrying out the invention in accordance with one form by way of example, see Figure 1, a revolution-counting mechanism for an electricity meter include a main train of digital indicating wheels in the form of an array of drums 11 to 15 which carry on their curved surfaces figures that indicate the count in decade form, drum 11 being the first wheel as above defined, that is the wheel that provides the display of the lowest numerical significance. The train is driven by a driving shaft 16 which is linked by gearing represented at 17 to the meter disc 18.

The mechanical connection (not shown) between shaft 16 and drum 11 should be understood as being of the kind, described above, which in order to allow the drums 12 to 15 to stopped accurately through all their digital readings necessitates the somewhat inaccurate continuous actuation of drum 11 over at least part of its range 2 to 8.

To shaft 16 is rigidly secured supplementary display means in the form of a drum 21 close to the right-hand side of drum 11 and marked on its courved surface with figures corresponding to those on drum 11 but of smaller size, in particular as regards width. The height of each figure of drum 21 is smaller too, but not sufficiently to prevent clear identification, at all times when the display of drum 21 is changing, of at least one of the two adjacent figures of drum 21 which are then only partly visible. Thus the figures on drum 21 indicate the angular position of shaft 16 precisely, in an analogue manner, whereas the figures on drum 11 indicate it inaccurately, over a part, at least, of each complete revolution of the driving shaft.

The overall display is as usual masked by a dial plate 22 — see Fig. 2 — having windows 11^1 to 15^1 to display the readings on drums 11 to 15 respectively. To display the reading of drum 21, window 11^1 for drum 11 is extended as at 21^1.

In operation, the supplementary indication given by drum 21 as viewed through the window extension 21^1 is so inconspicuous on account of its much smaller width and smaller hight compared with the main display of drums 11 to 15 to the eye of a subscriber making a casual reading for his own information as not to be included by him in that reading.

To an engineer reading the meter on site, on the other

hand, the supplementary display is clearly enough visible to be easily readable without unsealing the meter, and as drum 21 is located close to drum 11 this supplementary display is moreover easily readable by him in preference to the display of drum 11 whilst he is stationed to view the display of the remaining drums 12 to 15. Thus the mechanism of the invention facilitates the making of an accurate reading by a skilled observer without being likely to confuse a subscriber or orther unskilled observer who is making a casual reading of the digital display of the mechanism.

The invention is also applicable where the main train of indicating wheels is in the form of an array of four discs 31 to 34 (see Figs. 3 and 4) rather than the five drums 11 to 15 of Fig. 1. Here disc 31 is the first wheel, as above defined, corresponding to drum 11. Driving shaft 16 is now normal to the plane of the paper in Fig. 3 but is seen in the side view of Fig. 4, from which the mechanical connection whereby the shaft drives the first wheel — here disc 31 — is again omitted. To provide the supplementary display a disc 36 is secured to shaft 16 behind disc 31 from the point of view of an observer. Disc 36 is marked on that one of its plain surfaces which faces disc 31 with figures which correspond to the on disc 31 but which are of much smaller size and are located nearer the axis of shaft 16. To enable the figures on disc 36 to be seen, disc 31 is provided with suitably placed windows 38.

The dial plate 37, see Fig. 5, has the usual windows 31^1 to 34^1 to reveal the displays of the corresponding discs, window 31^1 being extended at 36^1 to display the reading of the supplementary disc 36, as seen through the appropriate aperture in disc 31.

The operation of this embodiment is the same in principle as that first described. An accurate analogue display of the first decade of the count is given to a skilled observer without having to unseal the meter, whilst this supplementary display is sufficiently inconspicuous as not to be mistakenly included by an unskilled observer in the reading given by the main discs.

In an alternative arrangement, not shown, disc 36 may be in front of disc 31 — that is, on the observer's side of disc 31. In this case the apertures in disc 31 are not necessary. Disc 36 must of course be of small enough diameter not to obscure the displays of disc 31 as seen through window 31^1.

In any of the above embodiments, the supplementary indicating wheel may be linked to driving shaft 16 through gearing rather than be rigid with it. This enables the supplementary display to be rendered inconspicuous by being detached somewhat from the main display.

In any of the above-described arrangements the supplementary indication may be rendered inconspicuous compared with the reading of the main train on other ways than difference in size.

As already stated, the invention is equally applicable where the count is displayed in other than decade form. Further, the invention is not limited in its application to electricity meters, but may be used wherever it is desired to afford facilities for measuring the rotation of a driving shaft by skilled and unskilled observers in the manner above described.

WE CLAIM :—

1. A revolution-counting mechanism including a main train of digital indicating wheels arranged to be driven by a driving shaft through a coupling to the first indicating wheel of the train-that is, the wheel of least numerical signification-, the coupling being such that said first wheel has an inaccurate response to the shaft rotation during a part at least of each complete revolution of the shaft, supplementary display means for providing an analogue indication which is always an accurate response to the shaft rotation, such analogue indication being visible to an observer stationed to view the display of the main train but being inconspicuous compared with that display.

2. A mechanism as claimed in claim 1 wherein said supplementary display means includes a supplementary indicating wheel rigid with the driving shaft.

3. A mechanism as claimed in claim 2 where said first wheel is of the drum kind carrying its figures on its curved surface, wherein said supplementary wheel also carries its figures on its curved surface and is disposed close to the right-hand side of said first wheel.

4. A mechanism as claimed in claim 2 where said first wheel is of the disc kind carrying its figures on one of its plain surfaces, wherein said supplementary wheel also carries its figures on one of its plain surfaces and is disposed on the observer's side of the first wheel in such manner as not to obscure the display of the first wheel.

5. A mechanism as claimed in claim 4 modified in that the supplementary wheel is disposed on the other side of the first wheel, which is provided with one or more windows through which the display of the supplementary wheel may be viewed.

6. A mechanism as claimed in any of the preceding claims wherein the analogue indication is rendered inconspicuous as aforesaid by being given in figures of smaller size than those carried by the main indicating wheels.

7. A revolution-counting mechanism substantially as hereinbefore described with reference to Figures 1 and 2 or to Figures 3 to 5 of the accompanying drawings.

R. HALL
of REMFRY & SON,
Agent for the Applicants.

Dated this 24th day of December 1960.

Printed by The Nelys Printing Works, Calcutta-1.

FERRANTI, LTD.
No. 74669 of 1960

1 Sheet.

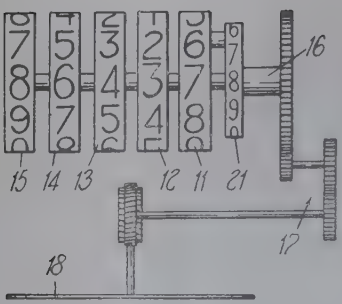

FIG. 1.

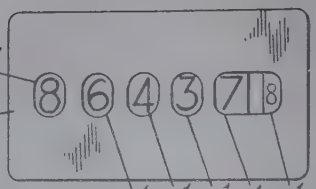

FIG. 2.

FIG. 4.

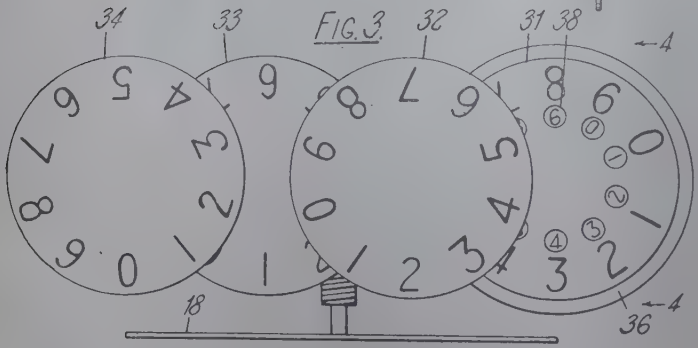

FIG. 3.

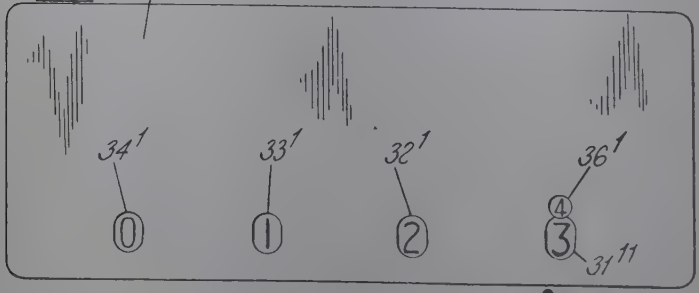

FIG. 5.

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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74670 filed 24th December 1960, 5 Paus 1882 (Saka). Reciprocity date (United Kingdom)—28th December 1959. (Accepted 14th May 1962.)

A PROCESS FOR THE PRODUCTION OF A NEW CELLULOSE ION-EXCHANGE MATERIAL.

GLAXO LABORATORIES LIMITED, A BRITISH COMPANY, OF GREENFORD, MIDDLESEX, ENGLAND.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

The present invention concerns improvements in or relating to cellulosic ion-exchange materials.

α-Cellulose powder has been modified by suitable treatment to yield products having anion or cation-exchange properties (Sobers and Peterson, J.A.C.S., 1954, 76, 1711-1712, ibid. 1956, 78(4), 751-755, Sobers et al, J.A.C.S., 1056 78(4), 756-763). One product having anion-exchange properties was obtained by treating strongly alkaline α-cellulose powder with 2-chloro-N,N-diethylethylamine. This product, referred to as DEAE-cellulose, has found application as an ion-exchange adsorbent for proteins and proteinaceous materials, e.g., enzymes, since relatively large amounts of protein may be adsorbed onto and eluted from DEAE-cellulose under mild conditions. α-Cellulose appeared particularly promising to the above workers because of its hydrophilic nature and large surface, the latter property being of importance in determining the adsorptive capacity of the modified DEAE-cellulose. The other factor affecting the adsorptive capacity of DEAE-cellulose is the number of active groups that can be introduced into the cellulose; experiments show, however, that the more diethylaminoethyl groups there are present, the more gelatinous and water-soluble becomes the cellulose so that in practice there is a limit to the number of ion-exchange groups which can be introduced, although diethylaminoethylation may not then be complete.

In the operation of ion-exchange processes on a commercial scale, it is generally preferable to employ a continuous, rather than a batchwise, process and, thus, in the case of DEAE-cellulose, it is desirable to have a material suitable for column operation. Ion-exchange materials suitable for commercial operation should thus posses, as far as possible, the following properties :

(1) A porous nature so that a large number of active groups is presented to the liquor being treated;

(2) A sufficiently open structure to permit a good flow of liquid through the column;

(3) An approximately standard particle size in order that, during packing of the column, the material is not segregated by differential sedimentation. A regular particle size also helps to prevent the occurrence of channelling and aids the maintenance of a regular flow throughout the cross-section of the column;

(4) The particles of the material should be sufficiently discrete, so that they do not clump or aggregate and so that the column of material may be back-washed and fluidised, for example to remove extraneous matter;

(5) The particles of the material should be sufficiently rigid in aqueous salt solutions and mild acid and alkaline reagents so that they maintain their physical form during adsorption, elution and regeneration and do not pack or settle to such an extent that the flow rate becomes impracticable.

DEAE-cellulose material as prepared by prior methods generally possesses the first of these properties but, because of its fine, slightly gelatinous, powder form, tends to clump very readily, cannot readily be backwashed and does not lead to a satisfactory flow rate. Furthermore, after a number of regenerations, it becomes too gelatinous to be of further use in a column.

Following research into the preparation of DEAE type ion-exchange material from a number of cellulose sources, we have discovered that one such source, namely balsa wood, enables a DEAE-cellulose ion-exchange material to be prepared which is satisfactory for operation in columns and to some extent approaches the desiderata for an ideal ion-exchange material mentioned above.

The present invention accordingly provides a process for the preparation of an ion-exchange material comprising balsa wood bearing diaminoethyl substituents in which balsa wood is reacted with an alkali metal hydroxide, the product obtained afterwards being reacted with a diethylhaloethylamine.

The present invention also provides as ion-exchange material, comprising balsa wood bearing diethylaminoethyl substituents, when prepared by the process described in the immediately preceding paragraph. This material we shall call "DEAE balsa" for the sake of brevity.

The material may be in any convenient form for example sheet form, although particulate form is preferred.

In the preparation of DEAE balsa the balsa wood is conveniently first processed into particles of a suitable size for use in an ion-exchange column before the introduction of the ion-exchange groups. The particles of balsa wood may be of any convenient size but perferably not larger than 10 B.S. mesh. We have found particles of between 16 and 60 B.S. mesh to be particularly satisfactory.

The balsa wood particles are then treated to introduce the diethylaminoethyl groups by any convenient method. They may, for example, be reacted with an alkali metal hydroxide followed by reaction with a diethylhaloethylamine, preferably in the form of a hydrohalide. It is particularly convenient to use caustic soda and diethylchloroethylamine.

The new ion-exchange material of this invention in general has a loose structure which is readily substituted by DEAE groups and which can be penetrated by molecules of substances to be adsorbed. Thus, particles of DEAE balsa in general present a large number of active groups to the liquor to be treated. For example, we have found that the ion-exchange material according to the invention can be prepared with exchange capacities of from about 0·3 to about 1·5 meq./g. (dry weight). Particularly useful material is that having an exchange capacity of from 0·6 to 1·5 meq./g. (dry weight). It should, however, be noted that if it is attempted to produce the new material with an exchange capacity much above 2 meq./g., the material may tend to gel or be water-soluble, as is the case with known DEAE-cellulose.

By suitable choice of particle size, a good flow of liquid through a column can be maintained and, in particular, better flow rates can be obtained than with DEAE-celluloses hitherto available.

DEAE balsa according to this invention in general possesses good stability, including stability to alkalis. It may be regenerated several times with little alteration in its properties, although change in volume may be observed, the flow rate, however, remaining in general fairly constant.

The DEAE balsa of this invention may be used for the adsorption of many substances. Thus, for example while it may generally be used wherever DEAE-cellulose has hitherto been used, e.g., for separation and purification of proteins, etc., we have found that the new material is very useful in the purification and or concentration of fungal α-amylase, the purification and or concentration of polyiomyelitis virus and the acids derived from Vitamin B_{12} by hydrolysis (by adsorption), and Vitamin B_{12} (by adsorption of impurities while the vitamin passes through the column). DEAE balsa is also useful for removing impurities from ostreogrycin factors A and B

Price : TWO RUPEES.

In order that the invention may be well understood, the following Examples are given by way of illustration only :

EXAMPLE 1

Preparation of DEAE balsa

Balsa sawdust (5 kg., 16-60 mesh) was mixed in a horizontal mixer with sodium hydroxide solution (26 l. 5·75N) for one hour. 2(N,N-diethyl)amino-ethyl-chloride (5 kg.) dissolved in water (7·5 l.) was added and the mixture stirred at room temperature for 16 hours. Hydrochloric acid (25 l., 5N) was added with cooling and the resultant slurry filtered and washed with water; this yielded DEAE balsa (5 kg., dry weight) having an exchange capacity of 1·38 meq./gm. (dry weight).

EXAMPLE 2

Use of DEAE balsa in the preparation of fungal α-amylase

Sufficient DEAE balsa (wet screened 16-26 mesh) was prepared to give a 5'8" bed in a 6" diameter glass column of total height 10 feet (bed volume approximately 31·2 l.). The bed was buffered with 2 bed volumes 0·045 M sodium phosphate to pH 6·5 at a flow rate of 1·25 bed volumes per hour. 8·5 bed volumes of fungal α-amylase broth, obtained by culturing *Aspergillus oryzae* (dextrinising acitivity 16·4 u/ml. i.e., total activity 4,320 kilo-units) previously adjusted to pH 6·5 were fed into the column at a rate of 1 bed volume per hour, followed by 1 bed volume water. The column effluent showed a total activity of 120 kilo-units (adsorption efficiency 97·2%). The adsorbed fungal α-amylase was recovered by washing with 1 bed volume 1·6M sodium acetate buffer pH 4·7, followed by a water wash of 0·65 bed volumes per hour. 1 bed volume of this eluate contained 3,615 kilo-units of dextrinising activity (86·5% recovery), representing an eightfold concentration). A further 420 kilo-units were recovered from the eluate representing a total elution recovery of 96%.

EXAMPLE 3

Isolation of acids obtained by hydrolysis of vitamin B_{12}

19·4 g. of vitamin B_{12} were dissolved in 4 litres of 0·1N hydrochloric acid. The solution was left for 23 hours at 37°C., then for 10 hours at room temperature. The coloured material was extracted with phenol, the extract was washed twice with its own volume of water, then the phenol was removed by ether extraction in the presence of water.

A column of DEAE balsa prepared from balsa sawdust of dry particle size of 16-40 mesh as described in Example 1 was set up in a 4½" diameter tube, to give a packed height of 10". The vitamin B_{12} hydrolysate was put onto the column, and followed by water, at a flow rate of about 2 litres per hour. Unchanged vitamin B_{12} passed through quickly into the effluent, leaving the acidic hydrolysis products adsorbed on the DEAE balsa.

The effluent, containing 11·5 g. vitamin B_{12} in a volume of 3 litres, was treated with 30 ml. of concentrated hydrochloric acid and left for 24 hours at 37°C., then for 10 hours at room temperature to obtain a further yield of the required acid. The solution was freed from mineral acid *via* phenol as above, and run through the same column, followed by water.

The effluent contained 6·75 g. of vitamin B_{12} in a volume of 2·8 litres. 4·6 g. vitamin B_{12} and 28 ml. concentrated HCl were added and the solution was left for 40 hours at 37°C. It was again extracted *via* phenol and put onto the same DEAE balsa column. The water effluent contained 6·1 g. of unchanged vitamin B_{12}. After washing with about 10 litres of water to remove the last traces of vitamin B_{12} the required monobasic acid (12·0 g.) was eluted with 10 litres of 0·01N sodium chloride. The corresponding dibasic acid (5·5 g.) was then eluted with 7 litres of 0·1 N sodium chloride.

EXAMPLE 4

Purification of Crude Vitamin B_{12} with DEAE balsa

Two experiments were performed using DEAE balsa obtained as described in Example 1 from balsa of dry particle size of 16-40 mesh.

The vitamin B_{12} preparation used in the experiments was a red solution containing between 0·2 and 0·25 g. of vitamin B_{12} and about seven grams of solids per litre.

(a) In the first experiment ten litres of this material were extracted into phenol-chloroform (2 : 1) and regenerated into about 1500 ml. of water by addition of acetone/ether (1 : 2) until all the colour passed into the aqueous layer on shaking. This solution, containing traces of phenol and small amounts of acetone and ether, and which was 60% pure as determined by colorimetric and total solids estimations, was passed through a 5" depth of DEAE cellulose in a 1" diameter chromatographic column at a rate of 500 ml. per hour. The effluent from this column (72% pure) was concentrated *in vacuo*, filtered through kieselguhr and crystallised from acetone. The crystals were dissolved in hot water and recrystallised.

(b) In the second experiment a further ten litres of the above partially purified preparation were adsorbed on a mixture of 150 g. of charcoal plus 30 g. of kieselguhr in a 3" chromatographic column. After washing with water 60% aqueous acetone was passed through the charcoal giving a 70% pure eluate. The acetone was removed with diethyl ether and the mainly aqueous solution containing the vitamin B_{12} was passed through a 4" depth of DEAE celulose in a 1" diameter chromatographic column at a rate of 500 ml. per hour The effluent (76% pure) was concentrated *in vacuo* and crystallised from acetone. The crystals were redissolved in hot water and filtered through kieselguhr before recrystallisation.

The crystals from these experiments and a check sample of normal production vitamin B_{12} were dried overnight at 105°C. under vacuum. The purities of the dried crystals determined by colorimetric assay of solutions of weighed amounts were 94% from the first experiment, 95% from the second and 92% for the check sample.

EXAMPLE 5

Purification of Type 1 Polio Virus

3 g. balsa wood DEAE prepared as described in Example 1 from balsa wood of particle size of 16-40 mesh were suspended in 0·02 *M* phosphate buffer (pH 7·0) to give a column 21×110 mm. The virus fluid used was Type 1, Titre : $10^{-7\cdot1}$ Monkey kidney antigen (M.K.) : 1/512. 5 ml. of the virus solution were passed through the column at 1·5-2·0 ml./minute and then developed with a 0·02 *M* phosphate buffer (pH 7·0). The "hold-up" liquid (30 ml.) was discarded, and the eluate then collected in about 5 ml. portions.

The results are shown below :

	Vol.	Titre : % activity	M. K. : % M. K.
Starting Material :	5 ml.	7·1 100	1/512 100
1st eluate	6.5 ml.	5.7 5	1/3 <1
2nd eluate	5.0 ml.	6.9 63	1/8 <2
3rd eluate	5.5 ml.	6.5 27.5	1/6 1
4th eluate	5.1 ml.	6.3 27.5	1/6 1
Total eluted :		123	<5

the four eluates contained all the input activity and less than 5% of the Monkey kidney protein antigen.

EXAMPLE 6

Use of Balsa DEAE Cellulose for Purification of E. 129

25 g. of ostreogrycin from which the Factor Z had been removed (using cellulose phosphate) was dissolved in 200 ml. of 70% methanol, and the solution passed through a column of Balsa DEAE cellulose 4" high in a column 2½" in diameter. The column was washed with 70% methanol until the effluent no longer gave a green colour reaction with ferric chloride, and the washings added to the eluate. The total methanol solution was then concentrated under reduced pressure to a volume of approximately 200 ml. and the precipitated pale yellow antibiotic mixture was recovered by filtration.

We claim :

1. A process for the preparation of an ion-exchange material comprising balsa wood bearing diaminoethyl substituents in which balsa wood is reacted with an

alkali metal hydroxide, the product obtained afterwards being reacted with a diethylhaloethylamine.

2. A process as claimed in Claim 1 in which the balsa wood is in particulate form.

3. A process as claimed in Claim 1 or Claim 2 in which the alkali metal hydroxide is sodium hydroxide.

4. A process as claimed in any of Claims 1 to 3 in which the diethylhaloethylamine is diethylchloroethylamine.

5. A process for the preparation of an ion-exchange material as claimed in Claim 1 substantially as herein described with reference to Example 1.

6. An ion-exchange material comprising balsa wood bearing diaminoethyl substituents when prepared by a process as claimed in any of the preceding claims.

7. An ion-exchange material as claimed in Claim 6 in particulate form.

8. An ion-exchange material as claimed in Claim 7 in which the particles are less than 10 B.S. mesh in size.

9. An ion-exchange material as claimed in Claim 8 in which the particles are between 16 and 60 B.S. mesh in size.

10. An ion-exchange material as claimed in any of the preceding Claims 6-9 having an exchange capacity of 0·3 to 1·5 meq./g. (dry weight).

11. An ion-exchange material as claimed in Claim 10 having an exchange capacity of 0·6 to 1·5 meq./g. (dry weight).

R. HALL

OF REMFRY & SON

Agent for the Applicants.

Dated this 24th day of December 1960.

MGIP Santh.—SL—102 Patent/62—10-6-63—100.

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74672, 24th December 1960, (3rd Pausa, 1882 Saka).
(Accepted 20th September 1962.)

PHOSPHORINE ESTERS AND PROCESS FOR OBTAINING THEM.

MONTECATINI SOCIETA GENERALE PER L'INDUSTRIA MINERARIA E CHIMICA, of 18 Via Filippo Turati, Milan, Italy, an Italian Company.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

The present invention relates to a new class of phosphorine esters, having the general formula shown in Figure 1 of the accompanying drawings, wherein R' and R" are alkyl radicals having from 1 to 5 carbon atoms, R' being different from or equal to R", X is an oxygen or sulphur atom; R, is hydrogen or an alkyl radical having from 1 to 5 carbon atoms, and Y is a simple or branched aliphatic hydrocarbon chain containing from 1 to 5 carbon atoms. All the compounds included in the above-mentioned general formula have an outstanding insecticidal activity both with respect to domestic parasites (for instance, flies) and with respect to agricultural pests (for instance aphides). Another interesting activity of these compounds is that against mites, in their various stages of development as well as against their eggs.

They can be used in various ways. Generally it is better to dilute them with solid, liquid or semisolid carriers, adding wetting, adhesive, dispersing or emulsifying substances.

They can also be distributed in the air by fumigation, or in the form of aerosols. Other compounds having an insecticidal activity (such as phosphactic esters, DDT and gramehexane) can also be added to the phosphoric esters of the invention.

Pesticidal compositions containing phosphorine esters of the abovementioned general formula have been described and claimed in the Indian Patent Application No. 32887, which has been divided out of the present Application.

The compounds having the abovementioned general formula are prepared by reacting a metallic compound of a dialkylthio- or dialkyldithio-phosphoric acid having the general formula shown in Figure 2 of the drawings, wherein R', R" and X are defined above and Me is an alkaline metal (for instance, sodium or potassium) or ammonium, with an alkylamide of a monohalogenated acetic acid, having the general formula shown in Figure 3 of the drawings, wherein R, and Y are as defined above and Hal is a chlorine, bromine or iodine atom.

Said halogen compounds can be obtained by reacting a cyanoalkylamine with a haloacetylating agent (for instance, monochloroacetyl-chloride or monochloroacetic anhydride).

The reaction is preferably carried out in the presence of a solvent for one or both reagents. Very suitable for this purpose are, for instance, aliphatic ketones having from 1 to 5 carbon atoms which allow separation of the by-products and facilitate the separation of the end product. Reaction takes place at room temperature; in certain cases it is convenient to heat, for a short time, to 50-60°C.

Sometimes it may be convenient to use more than the stoichiometric quantity of one reagent.

The metallic halide, which is formed as by-product, can be removed either by filtration or (when the final product is insoluble in water) by adding water causing the dissolution of the inorganic salt and of the eventual excess of metallic phosphate,as well as the simultaneous precipitation of the end product.

The separation of the end product can also be carried out by other known methods (solvent extraction, concentration, crystallisation or chromatographic column).

The products having the general formula shown in Figure 1 and defined hereinbefore, are oily liquids, or, in certain cases, crystalline products soluble in common organic solvents.

Some of these products, generally the monothio-derivatives, have a good solubility in water, which is useful for certain applications. The invention is illustrated but not limited by the following examples.

Example 1.

36 g of di-hydrates sodium O,O-dimethyldithiophosphate and 20 g of N-cyanomethylamide of monochloroacetic acid are mixed in 80 ml of acetone. The reaction mixture is then heated to 50-60°C and kept at room temperature for 3 hours, while frequently agitating it. The major part of the solvent is subsequently evaporated under reduced pressure and the residue is poured into 80 ml H_2O, wherefrom it is mixed again with 50 ml of methylene chloride and subsequently washed twice with H_2O (40 ml). It is then dried on $MgSO_4$ and evaporated under reduced pressure. The raw material thus obtained is purified, the by-products being removed by continuous extraction with *n*-hexane.

By maintaining the residue under vacuum until a constant weight was reached, 26.5 g of product are obtained in the form of a strawcoloured limpid oil, which solidifies, after a short time, at room temperature, yielding crystals having a m.p 38-40°C. (after crystallisation from ethyl acetate and petroleum ether), having the formula shown in Figure 4 of the drawings,
N calculated=11.02%
N found=11.04 to 11.00%.

Example 2.

20 g N-cyanomethylamide of monochloroacetic acid (melting point 89 to 89.5 C.) are added to a solution of 37 g potassium O,O-diethyldithiophosphate dissolved in 80 ml of acetone.

The reaction is slightly exothermic and rapid precipitation of KCl takes place. After leaving it at room temperature for 2 hours, the reaction mixture is poured into half a litre of H_2O, under agitation. An oily compound separates which solidifies completely after a short time. This compound, filtered by aspiration and thoroughly washed with water yields a white powder having a melting point of 70-71°C. The product obtained is subsequently dissolved at a mild heat in 70 ml of ethyl acetate. By adding 100 ml of petroleum ether and allowing it to crystallize, 31 g of a solid colourless crystalline product are obtained having a melting point of 71.5 to 72°C. and consisting of N cyanomethylamide of O,O diethyl - dithiophosphorylacetic acid having the formula shown in Figure 5 of the drawings,
N calculated=9.92%
N found=9.66 to 9.65%.

Example 3.

20.8 g of potassium O,O-diethylmonothiophosphate and 13.2 g of N-cyanomethylamide of monochloroacetic acid (melting point 89 to 89.5°C) are mixed in 60 ml of acetone. The mixture is slightly warmed up to favour the dissolution of the reagents and is then left to stand for 2 hours. It is then heated with weak refluxing of the solvent for 30 minutes, cooled and filtered by aspiration in the presence of a coadjuvant (for instance, Celite). The limpid filtrate is evaporated until a constant weight was reached under reduced pressure. 28 g of a limpid straw coloured oil remain consisting of N-cyanomethylamide of O,O-diethylmonothiophosphorylacetic acid having the formula shown in Figure 6 of the drawings.
N calculated=10.52%
N found=9.91 to 9.88%.

Example 4.

36.5 g of di-hydrated crystalline sodium O,O-dimethyldithiophosphate and 19 g of N-methyl-N-cyano-

methylamide of chloroacetic acid (boiling point at 0.4 to 0.5 mm Hg=135 to 140°C.) are mixed with 60 ml of acetone; the reaction is slightly exothermic. The reaction mixture is left to stand for 15 hours and then kept under reduced pressure in order to evaporate most of the solvent. The residue is poured into water, taken again with methylene chloride and washed with water.

Operating substantially as described in Example 1, 24 g of the desired product consisting of N-methyl-N-cyanomethylamide of O,O-dimethyl-dithiophosphorylacetic acid, having the formula shown in Figure 7 of the drawings, are obtained in the form of an oily liquid.

N calculated=10.41%
N found=9.80 to 9.60%.

Example 5.

35 g of potassium O,O-diethyldithiophosphate and 19 g of N-methyl-N-cyano-methylamide of chloroacetic acid (boiling point at 0.4 to 0.5 mm. Hg=135 to 140° C.) are mixed in 70 ml of acetone. The reaction is highly exothermic. The mixture is left o stand for 15 hours and then the KCl formed is filtered off. The filtrate is then evaporated under reduced pressure. The residue, diluted with a small amount of methyl chloride is then washed with H_2O. The organic solution, after having been dried is evaporated under reduced pressure. 35 g of oily liquid which remain as residue consist of the N-methyl N-cyanomethyl-amide of O,O-diethyldithiophosphorylacetic acid, and correspond to the formula shown in Figure 8 of the drawings.

Example 6.

27.2 g of potassium O,O-diethylmonothiophosphate and 19 g of N-methyl-N-cyanomethylamide of chloroacetic acid are mixed in 70 ml of acetone.

The reaction mixture is slightly warmed and then left standing for 15 hours.

After being filtered in the presence of a coadjuvant (for instance, Celite); the limpid filtrate is concentrated under reduced pressure until a constant weight is reached. 39 g of a straw-coloured oil remain as residue consisting of N-cyano-methyl-N-methylamide of O,O-diethylmonothiophosphoryl-acetic acid, having the formula shown in Figure 9 of the drawings.

Example 7.

52 g of crystalline di-hydrated sodium O,O-dimethyldithiophosphate and 32.1 g of raw N-ethyl-N-cyanomethylamide of chloroacetic acid are reacted at room temperature in 100 ml of acetone. After 3 days the solvent is evaporated and the residue is poured into 150 ml of H_2O, whereafter it is taken again with 75 ml of CH_2Cl_2 and then washed with H_2O. After drying and evaporation of the solvent, 38 g of a liquid straw-coloured oil are obtained which when further purified by continuous washing with n-hexane is reduced to 28.5 g. This product consists of N-cyanomethyl-N-ethyl-amide of O,O-dimethyldithiophosphorylacetic acid having the formula shown in Figure 10 of the drawings.

N calculated 9.92 %
N found=9.53 to 9.38%.

Example 8.

21.5 g of potassium O,O-diethyldithiophosphate and 16 g of raw undistilled N-ethyl-N-cyanomethylamide of chloroacetic acid are mixed in 50 ml of acetone. Reaction occurs with moderate development of heat. The mixture after standing for 2 hours, is filtered by aspiration from KCl and after having evaporated most of the solvent under reduced pressure, the remaining residue is poured into H_2O. The organic phase, after being dried with small quantity of methylene chloride, is washed again with H_2O. After evaporation of the solvent under reduced pressure 20 g of N-ethyl-N-cyanomethylamide of O,O-diethyldithiophosphorylacetic acid having the formula shown in Figure 11 of the drawings are obtained in the form of a limpid yellow coloured oil.

N calculated 9.92%
N found=9.7 to 9.58%.

Example 9.

20.8 g of potassium O,O-diethylmonothiophosphate and 16 g of raw N-ethyl-N-cyanomethylamide of chloroacetic acid are reacted in 60 ml of acetone. The mixture after having been slightly warmed is left to stand for 1 hour and then heated under mild refluxing for half an hour. In order to separate KCl the mixture is subsequently filtered in the presence of a coadjuvant (for instance Celite) and concentrated under reduced pressure until constant weight is reached thus obtaining 29 g of N-ethyl-N-cyanomethylamide of O,O-dietyl-monothiophosphorylacetic acid, in the form of a light yellow oil, having the formula shown in Figure 12 of the drawings.

Example 10

24 g of chloroacetic N-methyl-N-beta-cyanoethylamide (boiling point at 0.2 mm Hg=147°C) are added to 75 ml of a water solution of sodium O,O-dimethyldithiophosphate (concentration 2.5 mol/litre) while mechanically agitating the mixture. The temperature rises spontaneously up to about 45°C. After having been agitated for 24 hours the reaction mixture is extracted with 100 ml of CH_2Cl_2. The organic extract is washed twice with a total amount of 80 ml H_2O thus dried and evaporated under reduced pressure. The residue is purified by continuous washing with n-hexane.

After treatment under reduced pressure, 26.7 g of N-methyl-N-betacyanoethylamide of O,O-dimethyldithiophosphorylacetic acid are obtained in the form of an oily liquid, having the formula shown in Figure 13 of the drawings.

N calculated=9.92%
N found=9.32 to 9.29%.

Example 11.

37 g of potassium O,O-diethyldithiophosphate and 24 g of chloroacetic N-methyl-N-beta-cyanomethylamide (boiling point at 0.2 mm Hg=147°C.) are reacted in 75 ml of acetone. The reaction is so exothermic as to heat the mixture to a temperature at which the solvent is refluxed. After standing for 24 hours, most of the acetone is evaporated under reduced pressure, and the residue is poured into 100 ml of H_2O, wherefrom it is mixed with 60 ml of CH_2Cl_2. The organic phase is then washed twice with 50 ml of H_2O. After drying and evaporating under reduced pressure, 40.5 g N-methyl-N-beta-cyanoethylamide of O,O-diethyldithiophosphorylacetic acid are obtained in the form of a colourless limpid oil, having the formula shown in Figure 14 of the drawings.

P calculated=9.99 %
P found=9.35 to 9.32%.

Example 12.

21 g of potassium O,O-diethylmonothiophosphate and 16 g of chloroacetic N-methyl-N-beta-cyanoethylamide (boiling point at 0.2 mm Hg=147°C.) are reacted in 60 ml of acetone.

After having been mildly warmed the mixture is left to stand for 15 hours. The mixture is then filtered by aspiration in the presence of a coadjuvant (for instance, Celite) and evaporated under reduced pressure, thus obtaining as residue 29.5 g of N-methyl-N-beta-cyanoethylamide of O,O-diethylmonothiophosphorylacetic acid, in the form of a limpid oil, having the formula shown in Figure 15 of the drawings.

N calculated=9.52%
N found=9.16 to 9.17%.

Example 13.

48 g of crystallised di-hydrated sodium O,O-dimethyldithiophosphate and 32 g of N-alpha-cyano-isopropylamide of monochloroacetic acid (melting point 85 to 88°C) are reacted in 80 ml of acetone, heating initially to 40-50°C. After 3 hours most of the acetone is evaporated under reduced pressure, and the remainder is poured into 100 ml of H_2O, wherefrom it is taken again with 80 ml of CH_2Cl_2, then washed twice with 50 ml of H_2O, dried and evaporated under vacuum. The residue, consisting of a colourless limpid oil, is then purified by continuous washing with n-hexane. This residue,

after treatment under vacuum, consists of 32 g of a partially crystallised solid, having a melting point between 45 and 65°C., from which the desired product N-(alpha-cyano)-*isopropylamide* of O,O - dimethyl-dithiophosphorylacetic acid having the formula shown in Figure 16 of the drawings, can be obtained. The pure product has a melting point of 57 to 58°C. (from ethyl acetate and petroleum ether).

N calculated = 9.92%
N found = 9.89 to 9.70%.

EXAMPLE 14.

31 g of potassium O,O-diethyldithiophosphate and 20 g of chloroacetic N-(alpha-cyano)-*isopropylamide* (melting point 86 to 88°C.) are reacted in 80 ml of acetone. After heating initially up to about 50°C., the mixture is left to stand for half an hour at room temperature.

The reaction mixture is poured into 500 ml of iced water and the separating crystalline solid is filtered off and thoroughly washed with H_2O. 29 g of N-(alpha-cyano)*isopropylamide* of O,O - diethyldithiophosphoryl-acetic acid having the formula shown in Figure 17 of the drawings, are thus obtained in a form of a white crystalline solid having a melting point of 83 to 83.5°C. (from ethyl acetate and petroleum ether).

N calculated = 9.02%
N found = 9.00 to 8.98%.

EXAMPLE 15.

20.8 g of potassium O,O-diethylmonothiophosphate and 16 g of chloroacetic N-(alpha-cyano)*isopropylamide* are reacted in 60 ml of acetone. After heating initially to about 50°C., the mixture is left to stand for 15 hours. The mixture is then filtered by aspiration in the presence of a coadjuvant (for instance Celite). The limpid filtrate, evaporated under reduced pressure until a constant weight is reached, yields 26 g of N-(alpha-cyano)*isopropylamide* of O,O-diethylmonothiophosphoryl-acetic acid, having the formula shown in Figure 18 of the drawings, in a form of a yellow limpid oil.

N calculated = 9.52%
N found = 9.13 to 9.12%.

EXAMPLE 16.

34.6 g of potassium O-methyl-O-ethyl dithiophosphate and 19.9 g of N-cyano-methylamide of monochloroacetic acid are mixed in 120 ml of acetone; the mixture thus obtained is refluxed for 20 minutes and then left to stand for 15 hours. After this period the precipitated KCl is separated by filtration and most of the solvent is evaporated under reduced pressure. The residue is poured into 150 ml of water, taken again with 6 ml of methylene chloride and washed twice with water (50 ml each time). After drying on $CaCl_2$ and evaporation of the solvent under reduced pressure, 32 g of a slightly opalescent colourless oil which solidifies after a short time in the form of a waxlike solid, are obtained as a residue.

The product, crystallized from diluted methanol, and having a melting point of 54-58°C., substantially consists of N cyano-methylamide of O-methyl-O-ethyl-dithiophosphorylacetic acid, having the formula shown in Figure 19 of the drawings.

P calculated = 11.55%
P found = 11.12% - 11.07%.

EXAMPLE 17.

34.6 g. of potassium O-methyl-O-ethyl-dithiophosphate and 24 g of N-ethyl-N-cyanomethylamide of monochloro-acetic acid are mixed in 120 ml of acetone; the reaction is mildly exothermic.

By operating substantially as described in example 16, 30 g of a light yellow oil ($D_4^{20} = 1.200$; $n_D^{20} = 1.5262$) are obtained. It consists substantially of N-ethyl-N-cyanomethylamide of O-methyl-O-ethyl-dithiophosphoryl acetic acid, having the formula shown in Figure 20 of the drawings.

P calculated = 10.46%
P found = 10.72-10.69%.

EXAMPLE 18.

34.6 g of potassium O-methyl-O-ethyl-dithiophosphate and 24 g of N-methyl-N-beta-cyanoethylamide of monochloroacetic acid are mixed in 150 ml of acetone; the reaction is mildly exothermic. By operating substantially as described in example 16, 41.5 g of a colourless oil, having $D_4^{20} = 1.248$ and $n_D^{20} = 1.5353$, are obtained. This oil consists substantially of N-methyl-N-betacyano-ethylamide of O-methyl-O-ethyl-dithiophosphoryl acetic acid, having the formula shown in Figure 21 of the drawings.

P calculated = 9.46%
P found = 8.84-8.75%.

EXAMPLE 19.

23.1 g of potassium O-methyl-O-ethyl-dithiophosphate and 16 g of N-alpha-cyanoisopropylamide of monochloro-acetic acid are mixed in 100 ml of acetone. By operating substantially as described in example 16, 25 g of an oil having $D_4^{20} = 1.223$ and $n_D^{20} = 1.5233$, are obtained. This oil consists substantially of N-(alpha-cyano)-isopropylamide of O-methyl-O-ethyl-dithiophosphorylacetic acid having the formula shown in Figure 22 of the drawings.

P calculated = 10.46%
P found = 10.51%-10.47%.

We claim:

1. Process for the preparation of phosphorine esters comprised in the general formula shown in Figure 1 of the accompanying drawings, wherein R' and R'' are alkyl radicals having from 1 to 5 carbon atoms, R' being equal to or different from R''. R, is hydrogen or an alkyl radical having from 1 to 5 carbon atoms, Y is a simple or branched aliphatic hydrocarbon chain containing from 1 to 5 carbon atoms, and X is sulphur or oxygen, characterized by the fact that a metallic compound of a dialkylthio- or dialkyldithiophosphoric acid of the formula shown in Figure 2 of the drawings, where R', R'' and X have the abovementioned meaning and Me is an alkaline metal or ammonium, is reacted with an alkylamide or a monohalogenated acetic acid of the general formula shown in Figure 3 of the drawings, where R, and Y have the abovementioned meaning and Hal represents a halogen.

2. Process for the preparation of N-cyanoalkylamides of an O,O-dialkyldithiophosphoryl acetic acid according to Claim 1, wherein R' and R'' are methyl group.

3. Process for the preparation of N-cyanoalkylamides of O,O dialkyldithiophosphorylacetic acid according to Claim 1, wherein R' and R'' are ethyl groups.

4. Process for the preparation of N-cyanoalkylamides of an O,O-dialkyldithiophosphoryl acetic acid according to Claim 1, wherein R' is a methyl group and R'' is an ethyl group.

5. Process for the preparation of phosphorine esters according to Claims 1 to 4, wherein R, is selected from the group consisting of hydrogen, methyl and ethyl

6. Process according to Claim 1 for the preparation of N-methyl-N-cyanomethylamide of O,O-diethyldithiophosphoryl acetic acid.

7. Process according to Claim 1 for the preparation of N-cyanomethylamide of O,O-dimethyldithiophosphoryl-acetic acid.

8. Process according to Claim 1 for the preparation of N-ethyl-N-cyanomethylamide of O,O-diethyldithiophosphorylacetic acid.

9. Process according to Claim 1 for the preparation of N-(alpha-cyano) isopropylamide of O,O-diethyldithiophosphorylacetic acid.

10. Process according to Claim 1 for the preparation of N-cyano-methylamide of O-methyl-O-ethyl-dithiophosphorylacetic acid.

11. Process according to Claim 1 for the preparation of N-cyano-methylamide of O-methyl-O-ethyl-dithiophosphorylacetic acid.

12. Process according to Claim 1 for the preparation of N-ethyl-N-cyanomethylamide of O-methyl-O-ethyl dithiophosphorylacetic acetic acid.

13. Process according to Claim 1 for the preparation of N-methyl-N-betacyanoethylamide of O-methyl-O-ethyl dithiophosphoryl acetic acid.

14. Process according to Claim 1 for the preparation of N-(alpha-cyano)-isopropylamide of O-methyl-O-ethyl-dithiophosphoryl acetic acid.

15. Process according to Claim 1 characterized by the fact that it is carried out in the presence of a solvent for at least one of the reagents.

16. Process according to Claim 1, characterized by the fact that the solvent is an aliphatic ketone, containing from 1 to 5 carbon atoms.

17. Process according to Claim 1, characterized by the fact that it is carried out at a temperature between 10° and 100°C., preferably between room temperature and 60° C.

B. DEPENNING

OF CANTWELL & CO.,

Agent for the Applicants.

Dated this 24th day of December 1960

MCIPC—L—164 Patent—62—16-8-63—100.

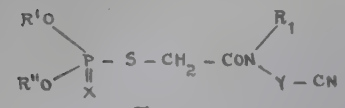

FIG. 1

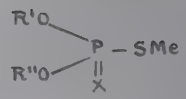

FIG. 2

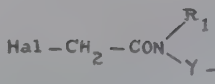

FIG. 3

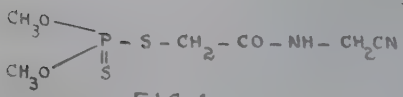

FIG. 4

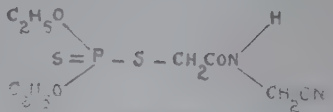

FIG. 5

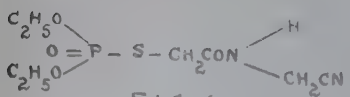

FIG. 6

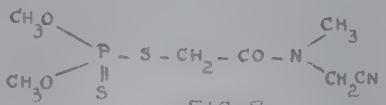

FIG. 7

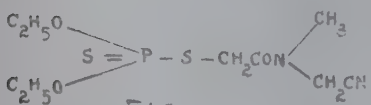

FIG. 8

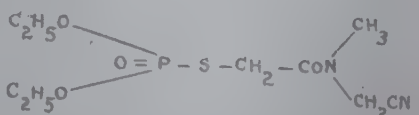

FIG. 9

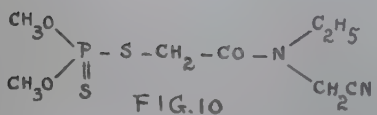

FIG. 10

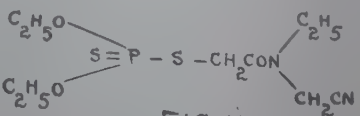

FIG. 11

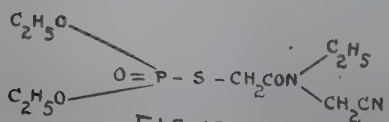

FIG. 12

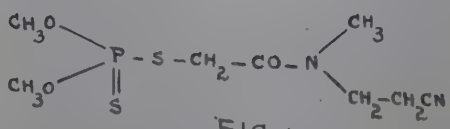

FIG. 13

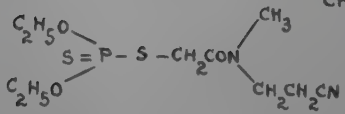

FIG. 14

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Agent for the Applicants.

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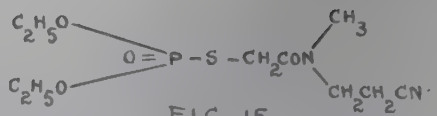

FIG. 15

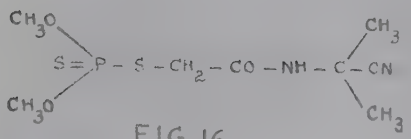

FIG. 16

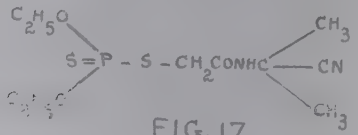

FIG. 17

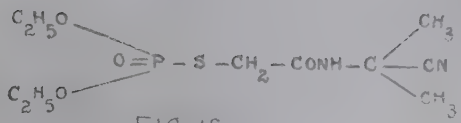

FIG. 18

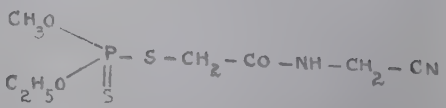

FIG. 19

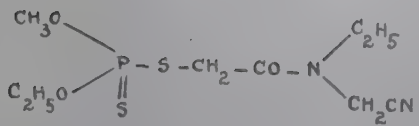

FIG. 20

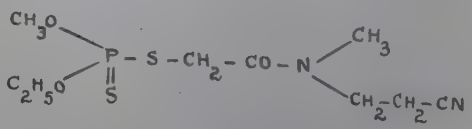

FIG. 21

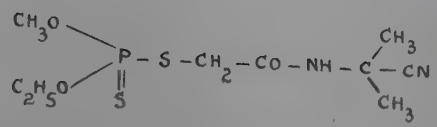

FIG. 22

B. Wetenning
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Agent for the Applicants.

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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74674, 24th December 1960, 3rd Paus 1882 (Saka). (Accepted 10th July 1962.)

STABILIZING HIGH MOLECULAR WEIGHT FORMALDEHYDE POLYMERS.

SOCIETA ITALIANA RESINE, an Italian Joint Stock Company, of 33, via Grazioli, Milan, Italy.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to stabilization of high polymers of formaldehyde by blocking the terminal hydroxyl groups through chemical reaction with a stabilizing agent.

It has long been known that high molecular weight polymers of formaldehyde can be stabilized by esterification of the terminal hydroxyl groups with acetic anhydride. This esterification confers to the treated polymers a high thermal stability. The abovementioned polymers can be stabilized also by esterification with methanol in the presence of an acidic catalyst (H. Staudinger "Die hochmolekularen organischen Verbindungen" Springer/Berlin 1932, page 230 and following pages, and J. F. Walker "Formaldehyde" Reinhold Publ. Corp., New York, 1953, pages 133-137). The known processes are objectionable under various aspects, for they should be carried out with a large excess of stabilizing agent which results in a high heat consumption and relatively heavy loss of reagent (acetic anhydride or methanol), the polymer moreover undergoing an appreciable degradation.

It has now been found that the terminal groups of high polymers of formaldehyde can be esterified under decidedly simpler and less expensive conditions by reacting the said groups with diazomethane in inert solvents in the presence of boron trifluoride and/or fluoboric acid or an agent capable of forming alkoxo-acids with the hydroxyl groups of the polymers. The resulting products exhibit at 222° C. a thermal stability constant lower than 1 per cent. per minute. The infrared spectrum analysis of the stabilized polymer no longer discloses any trace of free hydroxyl groups.

Generally, the reaction is carried out by suspending the high formaldehyde polymer in an inert solvent in the presence of 0.25 to 25 mol per cent. boron trifluoride and/or fluoboric acid and adding a solution of diazomethane in a suitable solvent, the temperature being kept within a range of −50° and +25° C. The reaction is pursued till a sharp yellow coloring of a persistent character is reached. The reaction product is filtered, the resulting polymer is suspended in 5 per cent. sodium carbonate solution, filtered and thoroughly washed with water to neutral reaction, whereupon it is dried in an oven at 45° C. at a reduced pressure. Alternatively, stabilization is carried out by reacting the high polymers before treatment thereof with diazomethane, with products, such as aluminium alcoholates which form together with the terminal hydroxyl groups alkoxo-acids, the latter being subsquently etherified with a diazomethane in an anhydrous inert medium. The latter reaction also is preferably carried out at the abovementioned temperatures.

The following examples are explanatory of the invention, but should not be understood as limitations thereof.

Example 1.

120 grams formaldehyde polymer of high molecular weight in a finely subdivided conditions, of about 2.6 viscosity (in a 0.5 per cent. solution in p-chlorophenol with 2 per cent. alpha-pinene, the viscosity being calculated as $\frac{\eta \text{ solution}}{\eta \text{ solvent}} - 1$) is suspended in 2 liters absolute ether in a 5 liters-flask provided with a stirrer, a funnel with a cock, gas bubbler and a condenser connected with a dehydrating trap. While vigorously stirring at 0° C. 0.7 grams boron trifluoride is added followed by the addition during 1½ hours vigorous stirring of 0.5 grams diazomethane dissolved in 500 cbc absolute ether. Stirring is pursued during further 20 minutes following the addition of diazomethane, whereupon the suspended product is filtered, washed with hot water and ultimately with methanol, and is dried in an oven at 45° C. at a reduced pressure. The resulting polymer is of a 2.5 viscosity (determined as explained above), and of thermal stability constant at 222° of 0.08 expressed as loss per cent per minute, determined by the method described by M. A. Naylor and A. W. Anderson in J. Am. Chem. Soc. 76 3962 (1954).

Example 2.

120 grams polyformaldehyde of high molecular weight in a finely subdivided condition of a 1.9 viscosity determined as explained in Example 1 is poured into a 3 liter flask equipped as explained in Example 1 containing 1 liter anhydrous tetrahydrofurane admixed with 0.9 grams fluoboric acid, the temperature of the reaction mixture being brought to −5° C. During 30 minutes while steadily stirring 0.7 grams diazomethane dissolved in 250 cbc anhydrous tetrahydrofurane are added. Stirring is pursued during further 30 minutes after completion of the addition of the diazomethane solution, whereupon the polymer is treated as indicated in Example 1. The stabilized polymer is of a 1.85 viscosity and a thermal stability at 222° C. of 0.1 per cent. per minute.

Example 3.

In a 3 liter flask having four necks equipped with a stirrer, a condenser connected with a dehydrating trap, a gas bubbler and a funnel with a cock, 120 grams polyformaldehye of high molecular weight and 3.5 viscosity, together with 1,500 cbc absolute ether are poured. The polymer should be finely pulverised. 7.5 mg aluminium tri-isobutylate are then added and stirring is continued at room temperature during 45 minutes. The reaction mixture is brought to 0° C., whereupon 0.7 grams diazomethane dissolved in 300 cbc absolute ether is introduced during 30 minutes while stirring. Stirring is thereafter continued during 45 minutes, the stabilized polymer being then treated as described in Example 1. The stabilized polymer is of a 3.3 viscosity and exhibits a heat stability constant at 222° C. of 0.07 per cent. per minute.

We claim:

1. Method for stabilizing formaldehyde polymers of high molecular weight, consisting in converting the terminal hydroxyl groups of the polymer to methyl ether groups by means of diazomethane either directly or by first reacting the polymer with compound capable of forming alkoxo-acids with said terminal groups and then etherifying the formed alkoxo-acids by diazomethane.

2. Method as claimed in Claim 1, wherein the polymer is suspended in an inert solvent and is reacted with diazomethane in the presence of a catalyst selected from the group consisting of boron trifluoride and fluoboric acid.

3. Method as claimed in Claim 1, wherein the compound capable of forming alkoxo-acids with the terminal hydroxyl groups of the polymer is an aluminum alcoholate.

4. Method as claimed in Claim 1, wherein the compound capable of forming alkoxo-acids with the terminal hydroxyl groups of the polymer is aluminum triisobutylate.

W. F. DePENNING

of DePENNING & DePENNING.

Agents for the Applicants.

Dated this 24th day of December 1960.

Price: TWO RUPEES.

MGIPC—S5—108 Patent/62—30-5-63—100.

INSPECTION

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74675, filed 24th December 1960 (3 Paus. 1882 (Saka).

(Accepted 11th January 1962.)

"A CONNECTING DEVICE FOR A FLUTED ROLLER SHAFT IN A SPINNING FRAME."

SIGEMATSU TAKITA, ENGINEER, OF No. 150, NANIWA-HONMACHI 3-CHOME, AMAGASAKI, JAPAN, JAPANESE SUBJECT.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This invention relates to a connecting device for a fluted roller shaft in a spinning frame. A fluted roller shaft consists of a number of short shafts or staffs connected together in alignment, and each staff generally provides 4 to 8 fluted rollers. Each staff is directly connected with next one, or is connected through the intermediary of a short spindle which serves as a journal for a bearing.

The main object of this invdntion is to obtain a connecting device which afford a means to tightly connect the short spindle with next staffs but can be easily disconnected from them.

Another object of this invention is to obtain an intermediate short spindle which provides a ball or roller bearing member encircling thereon, and the bearing member can be taken off endwise along the spindle when the spindle is disconnected from next staff.

According to this invention, an intermediate short spindle is connected with next staffs by a spline or polygon at one end and by a screw at the other end, and a bearing member provided thereon is held in its position by next staffs when they are connected. By this means, the bearing member can be taken off if the short spindle is disconnected at either end.

A spline or polygonal connection is rigid and steady, but the fitting surfaces wear off rapidly if the connection is frequently disconneted, whereby the connection becomes loose. A screw connection can be disconnected far easier than a spline or polygonal connection although rigidity of connection is not so good as a spline or polygonal connection. The connection of staffs, wherein the intermediate spindle is connected by a spline or polygon at one end and hy a screw at the other end, is more rigid than they are all connected by screws and can be disconnected easier than they are all connected by a spline or polygon.

According to this invention, the bearing member which encircles the spindle is held on a roller stand, so that the spindle is required to be frequently disconnected from the next staff for cleaning the bearing. In such a case the intermediate paindle is disconnected at the screw end keeping the spline or polygonal end untouched.

The invention will be further described in the following description reference being made to the accompanying drawing, wherein

Fig. 1 is a sectional front view of an intermediate spindle connecting a staff at each end thereof.

Fig. 2 is a plan view of an intermediate spindle in a reduced scale, and

Fig. 3 is a same view of two staffs connected at each end of an intermediate spiudle according to this invention.

In the drawing, 1 and 2 denote two staffs of a fluted roller shaft, said staffs being connected through the intermediary of a short spindle 3. As illustrated in Fig. 2, the intermediate spindle 3 is manufactured separately from the staffs, so that a special steel which is stronger and more wear-less than ordinary steel may be used. For this reason the spindle can ba made in a reduced diameter, so that a space for providing a ball or roller bearing is produced around the spindle. Each end 12 of the spindle is extended in a reduced diameter, and a screw thread 13 and a spline 14 are respectively provided on each extension. Balls or rollers 4 are hold in a retainer 5 and the retainer is inserted in a cylindrical holder 6, and is kept in its position by discs 7 with a spring ring 8. This ring is originally made in a diameter somewhat larger than the inner diameter of the holder and is cut off at one point and forcibly inserted in a groove with a semi-circular section provided on the inner surface of the holder and a similar groove on the outer surface of the disc 7 at each end so as to keep the outer ends of the retainer as shown in Fig. 1. A circular stuffing box 9 is inserted in the bore of holder, and a packing ring 10 is kept in the stuffing box, so that lubricant oil is prevented from leaking out of the bearing and dust is checked from entering into the bearing. The stuffing box has a cylindrical extension 9a at its outer end and is loosely inserted in a circular clearance in a ring 11, which is firmly fitted to each end of the staff, in order to make a detour to prevent free pass of dusts.

At each end of a staff is provided a hole at its center corresponding to the sizes of the before mentioned extension 12, and a negative screw is made at one end and a negative spline or polygon at the other end, each corresponding to the screw 13 and the spline or polygon 14 of the short spindle 3 respectively. When the spindle is connected with next staffs the bearing number is held on the spindle, and the cylindrical holder 6 is placed on the roller stand 15 of a spinning frame.

In the case of the bearing member is required to be taken out for inspection or cleaning, the short spindle is disconnected from next staff at the screw connection whereby the bearing member and the stuffing boxes can be removed from the spindle together with the holder 6.

Then the retainer 5 with the balls or rollers 4 can be removed from the holder pushing the disc 7 endwise, so that the spring ring 8 is slidden out of the semi-circular section grooves reducing its diameter against its own elasticity.

I CLAIM :—

A connecting device for a fluted roller shaft in a spinning-frame, comprising an intermediate short spindle to be connected between two staffs of the roller shaft having an extension of a reduced diameter at each end, and a screw and a spline or polygon being respectively provided at the extensions to connect with next staffs, and a ball or roller bearing member which encircles the intermediate spindle and is able to be taken off endwise along the latter, said bearing member being held between the ends of two staffs when they are connected with the spindle.

B. DePENNING
of DePENNING & DePENNING
Agent for the Applicant.

Dated this 24th day of December 1960.

Price : TWO RUPEES

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S. Takita.
No. 74675.

One Sheet.

Fig. 1

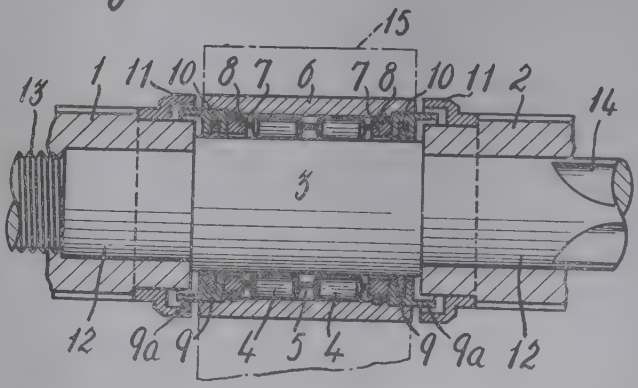


Fig. 2

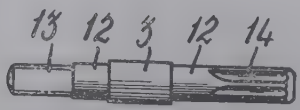
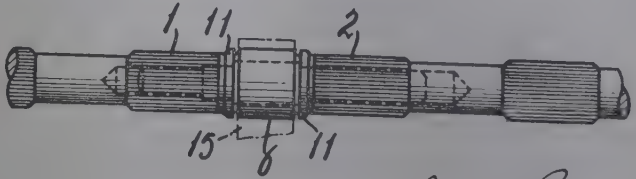


Fig. 3



B. DePenning

of DePENNING & DePENNING
Agents for the Applicant.

INSPECTION CENTRE

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74678. Application No. 74678, dated 26th December 1960.
Complete Specification left on 24th October 1961. (Application accepted 26th September 1962.)

PROVISIONAL SPECIFICATION

(Section 4)

" RETRACTABLE SUPPORTS OR BRAKE DEVICES FOR OPERATION OR SURGICAL TABLES : "

QUALITY INSTRUMENT CO., 184, Princess Street, City of Bombay, State of Maharashtra, India, an Indian Partnership Company, whose partners are Mohanlal Devchand Parikh and Kuchunalathu Pacru Bhaskaran Pillai, Indian Nationals.

The following Specification describes the nature of this invention :—

Operation tables or the like are usually provided with roller wheel to facilitate their being moved from place to place without being lifted or dragged about. To enable the said table or the like to be turned, normally one side of the table base is mounted on ordinary roller wheels which rotate in a fixed direction, while the other side of the table base is mounted on roller wheels which not only rottae, but are also capable of revolving on their pivots. Such type of swivel mounted roller wheels, known as the casters, aid the table or the like to be moved round corners.

When once kept inplace, it is necessary that the said table or the like does not thereafter shift about, a braking arrangement is, therefore, provided on such tables or the like whereby the swivel mounted roller wheels or the casters are lifted off the ground, so that the side of the table base comes to rest directly on the ground. The other side of the said table base which being mounted on ordinary roller wheels, is in this position quite steady, and does not permit any movement. When the said table is again required to be moved about the said casters are brought back to the working position, when the base of the said table, rests on roller wheels on one side and casters on the other side.

This type of braking arrangement is not found to be very satisfactory and effective as even in the braked state, one side of the said table, being mounted on roller wheels, the said table is liable to be moved if by accident any force is applied to the table. Further the easy movement of the table around corners is considerably reduced as the ordinary roller wheels of one side of the table base are found to offer considerable friction during movement.

It is the object of this invention to eliminate the aforesaid drawbacks and provide for an operation table or the like suitably mounted for easy movement, at the same time provided with a simple, yet highly effective braking arrangement.

This said table or the like according to the present invention is provided with casters (usually four in number) at the either sides of its base. The said casters, being capable of swivelling movements facilitate the said table to turn round very sharp corners with the least of strain.

The braking arrangement comprises of a device characterised in that it has two parallel plates, one above another in a horizontal plane, called the brake plates. The top and the bottom brake plates are capable of being brought close to each other, or being separated from each other with the aid of spring tension controlled by operating a lever.

A pair of brake plates are provided at the either side of the table base, and connected by means of a link bar. The base of the table is fixed to the top brake plates, and in the position when the two brake plates are brought close to each other, the casters povided at the table base touch the ground. In this position the table is not braked, and can be moved about easily on its casters.

When the table is to be braket, the top and the bottom brake plates are separated away from each other by means of the lever aperated externally at the table base, when the bottom brake plate touches the ground and thereby all the casters provided at the base of the table are raised off the ground level. In this position the table now rests on the bottom brake plates only, thereby forming a strong and steady base for the said table.

The top and bottom brake plates are guided towards and away from each other by means of two guide pins attached to one of the brake plates, which move in their guide sockets attached to the other brake plates.

When the table is to be moved about, the brakes are released and the casters brought back to their working position. The bottom brake plate recedes towards the top brake plate in this position, and the table rests on its casters.

QUALITY INSTRUMENT CO.,
of P. S. PAI & CO.
Authorised Agent.

Dated this 22nd day of December 1960.

COMPLETE SPECIFICATION

(Section 4)

Specification No. 74678.

" RETRACTABLE SUPPORTS OR BRAKE DEVICES FOR OPERATION OR SURGICAL TABLES : "

QUALITY INSTRUMENT CO., of 184, Princess Street, City of Bombay State of Maharashtra, India, an Indian Partnership Company, whose Partners are Mohanlal Devchand Parikh and Kuchunalathu Pacru Bhaskaran Pillai, Indian Nationals.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This invention relates to operation or surgical tables or the like, particularly to retractable supports or brake devices therefor. Such tables are generally provided with two pairs of rotatable wheels or rollers fixed to their bases and resting on the floor supporting them (the tables); such an arrangement facilitates moving such tables along the floor to their desired locations. However, the wheels fixed in position and oriented in a certain direction have certain disadvantages : for example, if the table is to be moved around other objects or around corners, some difficulty is experienced as the tables will have to be practically dragged around, which will leave marks on the floor and in the long run damage the wheel pivots and their supports. Such disadvantages have been sought to be overcome by providing at one end of the base of such a table a pair of swivellable wheels called casters, or castor wheels. When a table is to be moved around a corner or an object or along a curved path the caster wheels are first turned to the desired direction, and the table then pulled from that end or pushed from the other end. But the provision of a pair of castor wheels also does not prove

completely satisfactory, as the pair of fixed wheels still will have part sliding motion when the table is moved with the castors turned in a direction from that of the fixed wheels. The obvious solution is to provide only castor wheels supported from the base of such a table. However, such a step is also not satisfactory, whether an operation table is provided with only fixed wheels, castors or partly fixed wheels and partly castors, it is likely to be moved, however, slightly when a force is applied to the table. When the table is used during an operation, the effect of an inadvertently applied force can well be imagined.

After experiments with various mechanical devices, we have found that an operation or surgical table should be supported relatively firmly on the ground when it is put to its normal use and that it should be supported by at least two pairs of Castor wheels at other times for facilitating their movement from one location to another.

The principal object of this invention is to provide a surgical or operation table or the like with retractable supports which are easily actuated to engage the floor and support the table. A retractable support or a brake device for an operation or surgical table or the like according to my invention comprises a top plate fixed to the base of the table, a base plate or brake plate normally held at a predetermined distance therefrom by spring means provided therefor, and means for moving the base plate away from the base, the said spring means retracting the base plate to its normal raised position, when the said second mentioned means are returned to their normal nonactuated position.

In actual use at least two such devices are provided at the mid points of the opposite sides of the table, as the base plates can be made of sufficient width and length as to support the table without any danger of tilting abut them. The means for lowering the base plates of both the devices are connected together by a link bar so that they are actuated simultaneously when the said means provided on one of the devices is actuated. If desired, two pairs of such devices may be employed, the two of the devices of the opposite sides being linked together for simultaneous operation.

The invention will now be described in detail with reference to the accompanying drawings in which :—

Figure 1 illustrates a pair of the supports or brake devices according to our invention in elevation ;

Figure 2 illustrates the plan view of the devices or supports shown in figure;

Figure 3 illustrates the support or the brake device A on the left hand side of Figure 1, viewed in the direction of arrow X marked in figure 1.

The retractable support or brake device A (Figures 1 to 3) has a top plate 12 secured underneath the base of an operation or surgical table (not shown) and a base or brake plate 11. A pair of studs b, b' secured to the top plate 12 are engaged in tubular pieces a, a' secured to the brake or base plate 11 so that the plate 11 is guided in vertical direction when it is actuated downwards as described hereinafter; alternatively the studs may be secured to the base plate and the tubular pieces to the top plate. The top and the base plates 12 and 11 are further held in their normal position, shown in figures 1 and 2, by means of a spring 15 secured to a hook 14 on the top plate 12 and anchored at its lower end to the base plate 11. The top plate 12 has two downwardly depending bearing lugs o, o' formed with or secured to it; a pin or rod 13 is rotatably located in the bearings in these lugs; this pin also passes through and is secured to a circular hole in the eye d formed in the arm 1" of actuating lever 1 and another eye e formed in a bracket 2. The lever 1 has its two arms 1' and 1" formed at an acute angle ; the vertex of the lever 1 is forked (figure 3).

A wheel 5 is located between cheeks f and f' on the sides of the forked vertex of the lever 1 and held rotatably therein by means of a pin 6 having a head on one side for example, left hand side as shown in figure 3. This pin is retained in position by means of a spring clip 10 slipped into a groove at the other end of the pin 6. The cylindrical periphery of the eye d engages lower surface of the plate 12 tangentially. When the long arm 1' of the lever 1 is pulled down by means of its handle bar 8 the wheel 5 slides along a slide plate 4 onto the plate 11 thereby pushing it downwardly against the force of the spring 15 ; when the arm 1" is vertical, the plate 11 will be displaced to the greatest extent. On rotation of the eye d, when the lever 1 is actuated as mentioned above, the pin 13 secured to it is also rotated to the same extent; this pin being secured to the eye 2 of the bracket 2 also moves the lever end of the bracket; a link bar 9 fixed to the bracket 2 at its lower end is thus moved and it operates the actuating means of the device B which is described hereunder. When the lever 1 is pulled back to its position shown in figure 1, the wheel 5 is also pulled back over the slide plate 4 and the spring 15 retracts the brake or base plate 11. The slide plate 4 acts as a safety device against any accidental or unintentional operation of the lever 1. Due to the resistance offered by the slide plate 4 only a positive and firm operation of the lever 1 enables the wheel 5 to move either on or off the base or brake plate 11.

The device B is substantially similar to the device A except in so far as the actuating means are concerned. It also has got a top plate 12_1 and a brake or base plate 11_1, similar to the plates 12 and 11 of the device A, kept at predetermined distance apart and having a spring 15_1 secured to them. The actuating means of the device B are also similar to those of the device A except in that a lever similar to lever 1 is not provided in the device B; instead it has a bracket 3 corresponding to the short arm 1' and the vertex of the lever 1. This bracket 3 is secured by means of a pin or rod 13_1 to the top plate 12_1, just as the upper end of the short arm 1' of lever 1 of device A is secured by means of the pin 13 to the top plate 12; the lower forked end of the bracket 3 has a wheel 5_1 secured to it by means of a pin 6_1 retained in position by means of a spring clip 10_1 ; the right hand end of the link bar is secured to a bracket (not shown) corresponding to the bracket 2, fixed on the pin 13_1. When the lever 1 is actuated the right hand end of the link bar 9 moves the lower end of the bracket 3 and the wheel 5_1 ; as the bracket reaches its vertical position the brake or base plate 11_1 is pushed down. When the arm 1" of the lever 1 of device A and the bracket 3 are vertical the brake or base plates 11 and 11_1 will engegethe ground lifting and supporting the base of the table with the wheels or casters secured thereto above the ground. Thus the table is protected against any movement due to an accidental push or pull.

WE CLAIM :—

1. A retractable support or bracket device for an operation or surgical table or the like comprising a top plate fixed to the base of the table, a base plate or brake plate normally held at a predetermined distance therefrom by spring means provided therefor, and means for moving the base plate away from the base, the said spring means retracting the base plate to its normal raised position when the second mentioned means are returned to their normal non-actuated position.

2. A support or device as claimed in claim 1, in which the base plate and the top plate are held away at predetermined distance and are guided towards each other by means of studs secured to one of the said plates and tubular pieces secured to the other of the said plates, the studs engaging into the tubular pieces.

3. A support or device as claimed in claim 1 or claim 2, in which the top plate has two bearing lugs depending therefrom, a rod or shaft is rotatably supported in the bearing

holes formed in the said lugs, an actuating member having an eye at its upper end is fixed around the said shaft, a rotatable wheel is secured to the lower end of the actuating member, the said wheel bearing on and adapted to slide over the said base plate, and a bracket is fixed to the said rod or shaft.

4. A support or device as claimed in claim 3, in which the said actuating member is an arm of a bent lever, the other arm of the lever extending outwardly of the device.

5. A support of device as claimed in claim 3, in which the said actuating member is in the form of a link or bracket.

6. A surgical or operation table or the like having at least one support or device as claimed in claim 4, and at least another support or device as claimed in claim 5 the top plates of the two devices being secured to the base of the table exactly opposite to each other, the brackets fixed on the shafts or rods of the said two devices being connected together by means of a link bar, the arrangement being such that when the first device is actuated by means of the bent lever, the second device is also simultaneously actuated through the link bar.

7. A retractable support or a brake device for an operation or surgical table, substantially as herein described and illustrated in the accompanying drawings.

8. A surgical or operation table as claimed in claim 6 having supports which are substantially as herein described and illustrated in the accompanying drawings.

QUALITY INSTRUMENT CO.,
of P. S. PAI & CO.
Authorised Agent.

Dated this 23rd day of October 1961.

Printed by The Nelys Printing Works, Calcutta-1.

COMPLETE SPECIFICATION

QUALITY INSTRUMENT CO.,
NO. 74678 OF 1960

ONE SHEET

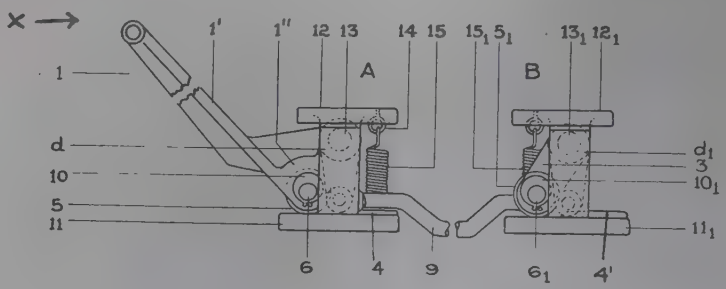


FIG. 1

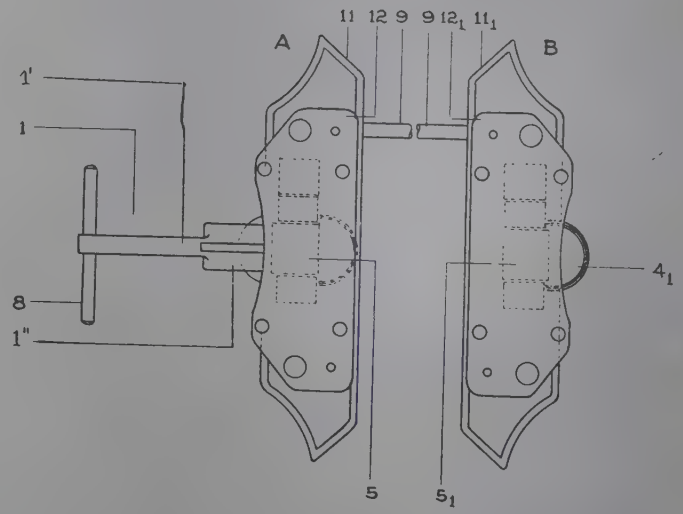


FIG. 2

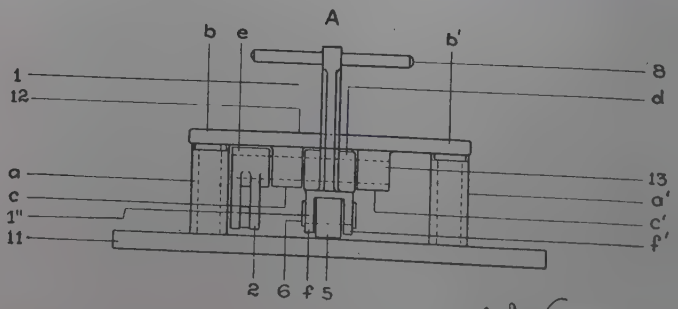


FIG. 3

P. S. PAI & CO.,
APPLICANTS' AGENT

INSPECTION

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.
Specification No. 74679. Application No. 74679, dated 26th December 1960.
Complete Specification left on 24th October 1961.
(Application accepted 26th September 1962.)

PROVISIONAL SPECIFICATION

(Section 4)

"HYDRAULIC ACTUATING SYSTEM FOR OPERATING TABLES OR THE LIKE."

QUALITY INSTRUMENT CO., OF 184, PRINCESS STREET, CITY OF BOMBAY, STATE OF MAHARASHTRA, INDIA, AN INDIAN PARTNERSHIP COMPANY, WHOSE PARTNERS ARE MOHANLAL DEVCHAND PARIKH AND KUCHUNALATHU PACHU BHASKARAN PILLAI, INDIAN NATIONALS.

The following Specification describes the nature of this invention :—

This invention relates to the hydraulic system used in operating tables or the like, wherein to suit the individual requirements, the height of the table and/or its tilt has often got to be varied and adjusted.

The known type of arrangements provided for the said purpose are not satisfactory in that they do not give efficient service and are often not smooth and easy to function, as usually mechanical devices in addition to the hydraulic, are made use of.

The present invention provides for a purely hydraulic system both for adjusting the height of the table or the like and also for adjusting the tilt of the table either towards the head-end or towards the foot end. A central oil-sump is provided in the table base and two hydraulic oil-pumps are used. One of the pumps is utilized to raise the vertical cylinder connected to the table proper, by hydraulic oil pressure, thereby increasing the height of the table. The second pump also operates another vertical cylinder hydraulically, which with the aid of a gear wheel, transmits the said vertical movement to tilt the table from the horizontal plane.

Separate release valves for the hydraulic systems of the said two cylinders are provided, by the operation of which, the hydraulic pressure can be released and the table brought back to the original position. Adjustments for the said release valves are also provided by which the force of release can be controlled either to a fast and quick drop in pressure, or to a steady and slow decrease in pressure.

QUALITY INSTRUMENT CO.,
of P. S. PAI & CO.,
Authorised Agent.

Dated this 22nd day of December 1960.

COMPLETE SPECIFICATION

(Section 4)

Specification No. 74679.

"HYDRAULIC ACTUATING SYSTEM FOR OPERATING TABLES OR THE LIKE."

QUALITY INSTRUMENT CO., OF 184, PRINCESS STREET, CITY OF BOMBAY, STATE OF MAHARASHTRA, INDIA, AN INDIAN PARTNERSHIP COMPANY, WHOSE PARTNERS ARE MOHANLAL DEVCHAND PARIKH AND KUCHUNALATHU PACHU BHASKARAN PILLAI, INDIAN NATIONALS.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This invention relates to hydraulic actuating systems employed in surgical operation tables and chairs. Modern surgical tables generally have two or more hinged portions called trunk sections, a head section which can be adjusted in height, a separately adjustable back elevator and a foot rest which can be secured as an extension to the trunk section, remote from the head rest. Different mechanisms actuated either, hydraulically or mechanically are provided for the adjustment of the different sections, namely to perfectly horizontal positions at different heights, Trendelenburg positions namely with the head or foot end inclined to the horizontal plane or with all the sections inclined from one side to the other, as may be necessary.

The object of this invention is to provide simple hydraulic system to adjust the height of the platform comprised by the different sections as well as to adjust the platform to the Trendelenburg positions.

A hydraulic actuating system, according to the invention for an operation or surgical table comprises two separate units, one for adjusting the height of the operation platform of the table and the other for tilting the platform to either of the two Trendelenburg positions namely the head end tilted down or the feet end tilted down positions, each of the said units comprising a spring biased plunger or piston actuatable by a foot pedal, housed in a pump cylinder communicating on the one hand with an oil reservior and on the other hand with a hydraulic ram ; the hydraulic ram of the first unit being arranged to raise the operation platform of the table, while the hydraulic ram of the second unit being arranged to tilt the said platform towards the head end or the foot end, as the case may be, and means for releasing the oil under pressure from the said units back to the reservoir.

The hydraulic ram of the first unit is connected to the operation platform of the table by means of a universal joint ; the hydraulic ram of the second unit is connected to the said platform by means of a rack and pinion device, the pinion being preferably formed as a sector shaped gear. The pressure release means comprise two separate release valves operatable by means of separate foot pedals.

In the accompanying drawings only those portions of the operation table as are necessary for the understanding of this invention are illustrated ; in these drawings,

Figure 1 illustrates a longitudinal section of the pedestal support of the operation table ;

Figure 2 illustrates an elevation of the lower portion of the body of the pedestal only,

Figure 3 illustrates top plan view of the lower portion of the body shown in figure 2, viewed along the lines X–X of figure 1,

Figures 3A and 3B illustrate sectional views along the lines A–A and B—B respectively of figure 3,

Figure 4 illustrates the pedestal in perspective.

Price : TWO RUPEES.

The pedestal of a surgical table consists of a base II body portion I and a neck portion III (figure 1). Within the body portion I, the two units of the hydraulic system are mainly housed. The pump cylinder 2′ of the first unit has a reciprocatable plunger or piston 2 in it. The piston 2, at its upper end, is connected to a spring 6 which is anchored at its upper end. A cranked lever Cr pivoted at one end Cr′ (figure 1) is connected to the piston 2 and to the spring 6; it is adapted to be oscillated by means of a foot pedal 7 provided at its free end, for the purpose of reciprocating the piston 2 in its cylinder 2′; when the piston 2 is reciprocated, the cylinder 2′ draws in oil from the oil reservoir R in the lower portion of the body I, through an inlet A, during the upstroke of the piston, and discharges it through an outlet B to inlet C of the ram cylinder 3′. Conventional types of valves (not shown) are provided in the inlet A and outlet B in the known manner. By actuating the pedal a number of times part of the oil in the reservoir R is delivered to the cylinder 3′; this oil raises the ram 3 upwardly thus raising the operation platform of the table (not shown) to the desired height. For lowering the platform a release valve 8 is provided; this valve when actuated by means of a pedal 11 opens an outlet 9, permitting flow of the oil under pressure in the unit through a hole E, back into the reservoir. By cautiously actuating the pedal 11 the platform can be lowered to the desired extent. The valve 8 can be adjusted by means of a screw 10 so as to release the oil under pressure in the unit slowly or quickly.

The second unit of the system is similar to the first unit, the pump piston 2_1 of the second unit is reciprocated in its pump cylinder $2'_1$ by the foot pedal 7_1; a spring 6_1 corresponding to the spring 6, connected to the cranked lever of the pedal 7_1 returns the piston 2_1 and the pedal 7_1 to their top positions when the foot is released from the pedal. During the upward strokes of the piston 2_1, the cylinder draws in oil from the reservoir R through inlet A_1 and during the downward strokes of the piston, the cylinder delivers oil under pressure to inlet C_1 of the ram cylinder 4_1 through an outlet B_1 and pipe or hose D_1. The oil under pressure delivered to the ram cylinder 4_1 raises the ram 4. This ram is either provided with or formed integral with a gear rack 5_1 engaging a sector gear pinion 5 fixed on a shaft 5_{11} provided on the platform; the shaft 5_{11} when turned about its axis tilts the platform so that one end for example, the head end is raised. The pressure in the ram cylinder is released by actuating a release valve 8_1 by means of a pedal 11_1 similar to the pedal 11 of the first unit when the outlet 9_1 is opened and the oil under pressure flows through the hole E_1. The valve 8_1 may be adjusted for quick or slow release by means of a screw 10_1 corresponding to the screw 10 of the valve 8 of the first unit. When the ram 4 is at a predetermined position in its cylinder 4_1 the platform will be horizontal; further release of oil under pressure from the cylinder 4_1 will tilt the platform in the other direction for example raise the head end of the platform upwardly. The inlet and outlet of the pump cylinder $2'_1$ is provided with valves (not shown), in the known manner.

WE CLAIM :—

1. A hydraulic actuating system for an operation or surgical table comprising two separate units, one for adjusting the height of the operation platform of the table and the other for tilting the platform to either of the two Trendelenburg positions namely the head end tilted down or the feet end tilted down positions, each of the said units comprising a spring biased plunger or piston actuatable by a foot pedal, housed in a pump cylinder communicating on the one hand with an oil reservoir and on the other hand with a hydraulic ram; the hydraulic ram of the first unit being arranged to raise the operation platform of the table, while the hydraulic ram of the second unit being arranged to tilt the said platform towards the head end or the foot end, as the case may be, and means for releasing the oil under pressure from the said units back to the reservoir.

2. A hydraulic system as claimed in claim 1, in which the piston or the plunger in the pump cylinder of each of the said units is connected to a spring anchored at its upper end, and a pivoted crank lever adapted to be depressed by means of a foot pedal, the spring serving to return the plunger or piston to their top positions.

3. A hydraulic system as claimed in either of the preceding claims, in which the said means for releasing oil under pressure from each said unit comprises a release valve adapted to be operated by a foot pedal and to be set for quick or slow release.

4. A hydraulic system as claimed in any of the preceding claims, in which the hydraulic ram of the said first unit is connected to the said operation platform by means of a universal joint.

5. A hydraulic system as claimed in any of the preceding claims, in which the hydraulic ram of the second unit is formed or provided with a gear rack engaging a sector shaped gear pinion fixed on a shaft secured to the said platform, the arrangement being such that when the said ram is raised in its cylinder the turning movement of the said pinion tilts the platform in the desired direction.

6. A hydraulic system as claimed in claim 5, in which the ram of the second unit is arranged to bring the platform to its horizontal position when it (the ram) is at a predetermined position in its cylinder and to tilt the platform in the reverse direction when it is lowered beyond the said predetermined position.

7. A hydraulic actuating system for an operation or surgical table, substantially as herein described and illustrated in the accompanying drawings.

8. An operation or surgical table provided with a hydraulic system as claimed in claim 7.

QUALITY INSTRUMENT CO.,
of P. S. PAI & CO.,
Authorised Agent.

Dated this 23rd day of October 1961.

Printed by The Nolys Printing Works, Calcutta-1.

COMPLETE SPECIFICATION

QUALITY INSTRUMENT CO.,
NO. 74679 OF 1960

NO. OF SHEETS : TWO
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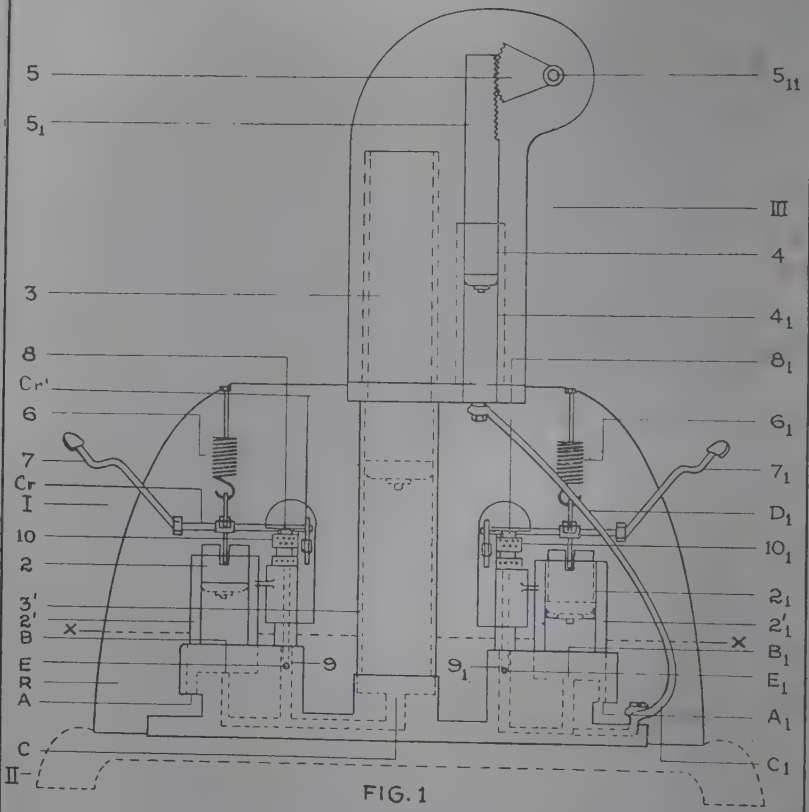


FIG. 1

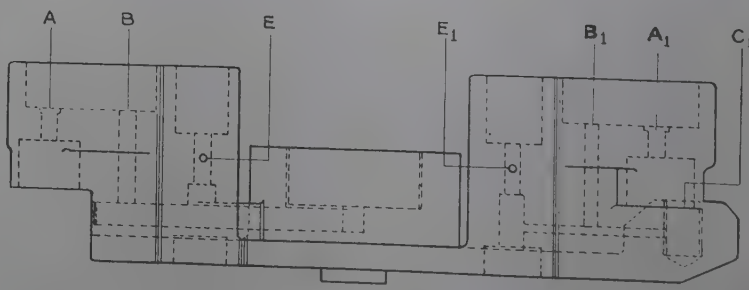


FIG. 2

of P. S. PAI & CO.,
APPLICANTS' AGENT

QUALITY INSTRUMENT' CO.,
NO. 74679 OF 1960

NO. OF SHEETS : TWO
SHEET NO. TWO

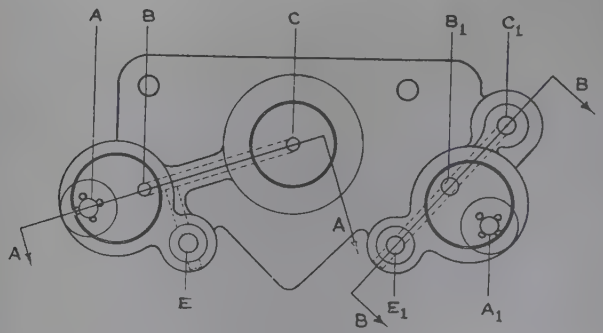


FIG. 3

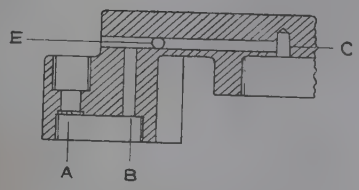


FIG. 3A

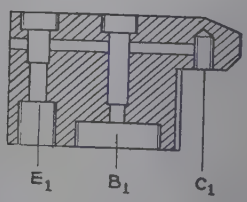


FIG. 3B

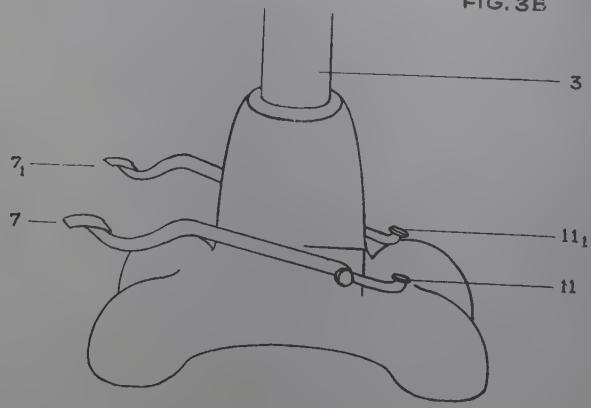


FIG. 4

of P. S. PAI & CO.,
APPLICANTS' AGENT

Per INSPEC

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74680, Application No. 74680 dated 26th December 1960. Complete Specification left on 22nd September 1961. (Application accepted 24th May 1962.)

PROVISIONAL SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO ELECTROLYTIC DERUSTING OF CORRODED METAL PARTS.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Old Mill Road, New Delhi-1, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification describes the nature of this invention.

This is an invention by KUMMATTITHIDAL SANTHANAM RAJAGOPALAN, NARAYANASWAMY SUBRAMANYAM, YELLAMRAJU VENKATA POORNA RAMCHANDRA RAO, all of the Central Electrochemical Research Institute, Karaikudi, Madras, India, all are Indian citizens.

This invention relates to improvements in or relating to the derusting and reclamation of rusted metal stores. Derusting is usually done by wire brushing, sand or grit blasting, tumbling, flame cleaning, sodium hydride descaling, acid pickling as well as by electrolytic derusting in acid, neutral and alkaline solutions. The present invention makes particular reference to reclamation by electrolytic derusting of rusted engineering stores, ferrous and non-ferrous, using neutral salt solutions.

The object of the present invention is to provide a method rapidly reclaiming derusted engineering stores by an electrolytic process involving the use of a cheap and readily available electrolyte, *e.g.*, sea water, solutions of common salt.

We have found that under appropriate process conditions rusted engineering stores, in particular, costly items having comparatively small surface area, *e.g.*, machinery parts, can be satisfactorily derusted in the course of several minutes *e.g.*, 5, 10, 20, or 30 minutes, with an electrolyte consisting mainly of common salt solution ; where available, sea water can also be used for this purpose. While electrolytic derusting in an inexpensive electrolyte like sea water has been attempted earlier with respect to oil tanks, ship bottoms and other rusted machinery and several commercial processes patented particularly in United States, it was always found that derusting in this electrolyte resulted in a surface carrying a black residual deposit which could not be removed and the derusting had to be carried out over a long period of *e.g.*, several hours to days. The process which is being patented has overcome these difficulties and the inventors claim that derusting can be carried out in such a simple inexpensive electrolyte like common salt solutions or sea water to a stage where completely rust free bright metal surfaces are obtained and the process time is shortened to as little as a few minutes, the actual time being determined in a trial experiment.

The new process for which protection is sought in this specification consists in raising electrolyte temperature, making the article to be derusted alternately cathode and anode, and passing a very heavy D. C. current, which conditions are very different from those employed in earlier processes. Under these conditions, the derusting proceeds to a stage where the article is made completely rust free. To facilitate wetting of the article a small quantity of a wetting agent may be added to the electrolyte, if necessary. Since the current required cannot be easily calculated in the case of intricate parts, the voltage drop in the solution can be used to control current density.

The effectiveness of the above method is compared with results obtained under conditions employed in older processes in the following Table. 3 per cent. common salt solution is used as the electrolyte and the total duration for cleaning was kept constant at 20 minutes.

PROCESS CONDITIONS	°C*	OBSERVATIONS.
1. Cathodic cleaning at room temperature at current densities ranging from		
(a) 0— 50 amps/sq. ft	30°	Partially cleaned. Patches of black deposit which cannot be removed by brushing left.
(b) 50—100 amps/sq. ft		
2. Anodic cleaning at room temperature at current densities ranging from		
(a) 0— 50 amps/sq. ft.	30°	Cleaning is even less satisfactoiy than in (1)
(b) 50—100 amps/sq. ft.		—do—
3. Anodic cleaning (10 minutes) followed by Cathodic cleaning (10 minutes) at room temperature at current densities ranging from	30°	
(a) 0— 50 amps/sq. ft.	—	Extent of cleaning similar to (1)
(b) 50—100 amps/sq. ft.		—do—
4. Cathodic cleaning followed by anodic cleaning at room temperature at current densities ranging from		
(a) 0— 50 amps/sq. ft.	30°	Extent of cleaning is improved, but black deposit left.
(b) 50—100 amps/sq. ft.		—do—
5. Cathodic cleaning followed by anodic cleaning at		
400 amps/sq. ft	(a) 30°	Part of the surface becomes bright but cleaping is incomplete.
	(b) 60°	—do—
	(c) 90°	Complete cleaning of all surface including grooves to get bright surface.

*Initial Temperature.

The inventors have further found that a large number of small items can be satisfactorily derusted several at a time by suspending them in a suitable basket which is connected to the source of supply. No special arrangements for agitation of the electrolyte is necessary.

The derusting process for which protection is sought under the specification leaves a metal surface which is much less prone to subsequent rusting as compared to acid pickling, which is a definite advantage from the point of view of subsequent preservation, storage and use of the items.

The cost of derusting and reclamation of engineering stores by the process outlined above compares favourably with other methods of cleaning, in particular chemical cleaning and electrolytic cleaning using other proprietary and nonproprietary processes.

The process for which protection is sought in the specification can also be extended to the cleaning of metal sheets and large size stores wherever power is available at sufficiently cheap rates.

R. BHASKAR PAI,
Patents Officer.
Council of Scientific & Industrial Research.

Dated this 17th day of December 1960.

Price : TWO RUPEES.

COMPLETE SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO ELECTROLYTIC DERUSTING OF CORRODED METAL PARTS.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OLD MILL ROAD, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

THIS IS AN INVENTION BY KUMMATTITHIDAL SANTHANAM RAJAGOPALAN, NARAYANASWAMY SUBRAMANYAM, YELLAMRAJU VENKATA POORNA RAMCHANDRA RAO, ALL OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI, MADRAS, INDIA, ALL ARE INDIAN CITIZENS.

This invention relates to improvements in or relating to the electrolytic derusting of corroded metal parts and reclamation of rusted metal stores. Derusting is usually done by wire brushing, sand or grit blasting, tumbling, flame cleaning, sodium hydride descaling, acid pickling as well as by electrolytic derusting in acid, neutral and alkaline solutions. The present invention makes particular reference to reclamation by electrolytic derusting of rusted engineering stores, ferrous and nonferrous, using neutral salt solutions.

The object of the present invention is to provide a method of rapidly reclaiming rusted engineering stores by an electrolytic process involving the use of a cheap and readily available electrolyte *e.g.*, sea water, solutions of common salt.

The invented method of electrolytic derusting of metal parts using a cheap and readily available electrolyte, *e.g.*, sea water, solutions of common salt, consists in passing a heavy direct current of electricity through the metal article immersed in the hot electrolyte, initially making the article cathodic and then anodic.

We have found that under appropriate process conditions rusted engineering stores, in particular, costly items having comparatively small surface area, *e.g.*, machinery parts, can be satisfactorily derusted in the course of several minutes *e.g.*, 5, 10, 20, or 30 minutes, with an electrolyte consisting mainly of common salt solution ; where available, sea water can also be used for this purpose. While electrolytic derusting in an inexpensive electrolyte like sea water has been attempted earlier with respect to oil tanks, ship bottoms and other rusted machinery and several commercial processes disclosed particularly in United States, it was always found that derusting in this electrolyte resulted in a surface carrying a black residual deposit which could not be removed and the derusting had to be carried out over a long period of *e.g.*, several hours to days. The process which is being patented has overcome these difficulties and the inventors have found that derusting can be carried out in such a simple inexpensive electrolyte like common salt solution or sea water to a stage where completely rust free bright metal surfaces are obtained and the process time is shortened to as little as a few minutes, the actual time being determined in a trial experiment.

The effectiveness of the above method is compared with results obtained under conditions employed in older processes in Table: 2. 3 per cent. common salt solution is used as the electrolyte and the total duration for cleaning was kept constant at 20 minutes.

PROCESS CONDITIONS	°C*	OBSERVATIONS.
1. Cathodic cleaning at room temperature at current densities ranging from		
(a) 0— 50 amps/sq. ft.	30°	Partially cleaned. Patches of black deposit which cannot be removed by brushing left.
(b) 50—100 amps/sq. ft.		
2. Anodic cleaning at room temperature at current densities ranging from		
(a) 0— 50 amps/sq. ft.	30°	Cleaning is even less satisfactory than one.
(b) 50—100 amps/sq. ft.		
3. Anodic cleaning (10 minutes) followed by cathodic cleaning (10 minutes) at room temperature, at current densities ranging from		
(a) 0— 50 amps/sq. ft.	30°	Extent of cleaning similar to 2.
(b) 50— 100 amps/sq. ft.		

*Initial Temperature.

PROCESS CONDITIONS	°C*	OBSERVATIONS.
4. Cathodic cleaning followed by anodic cleaning at room temperature at current densities ranging from		
(a) 0— 50 amps/sq. ft.	30	Extent of cleaning is improved, but black deposit left.
(b) 50—100 amps/sq. ft.		
5. Cathodic cleaning followed by anodic cleaning at		
400 amps/sq. ft. (a)	30°	Part of the surface becomes bright but cleaning is incomplete.
(b)	60°	Do—
6. Cathodic cleaning followed by anodic cleaning at		
400 amps/sq. ft.	30°	Complete cleaning of all surface including grooves to get bright surface.

The inventors have found that derusting process for which protection is sought under the specification leaves a metal surface which is much less prone to subsequent rusting as compared to acid pickling which is a definite advantage from the point of view of subsequent preservation, storage and use of the items.

The inventors have also found that the cost of derusting and reclamation of engineering stores by the process outlined above compares favourably with other methods of cleaning, in particular, chemical cleaning and electrolytic cleaning using other proprietory and non-proprietory processes.

We claim:

1. A method of electrolytic derusting of metal parts using a cheap and readily available electrolyte, *e.g.*, sea water, solutions of common salt, which consists in passing a heavy direct current of electricity through the metal article immersed in the hot electrolyte, initially making the article cathodic and then anodic.

2. A method as claimed in Claim 1 wherein a wetting agent is added to the electrolyte.

3. A method as claimed in Claim 1 or 2 wherein the following process conditions are representative of those that can be employed.

Electrolyte	:	3% Common salt solution.
Duration	:	20 minutes.
Sequence of steps	:	The article to be derusted is initially made the cathode while passing direct electric current for 10 minutes and then made the anode for 10 minutes.
Current density	:	400 amps/sq. ft. of the surface of the article to be derusted.
Temperature to which the bath is to be heated initially and at which it is to be maintained	:	90°C.

4. A method as claimed in any of the preceding claims wherein a large number of small items are derusted several at a time by suspending them in a suitable basket which is connected to the source of supply.

5. A method of electrolytic derusting of metal parts substantially as hereinbefore described.

R. BHASKAR PAI.

Patents Officer,

Council of Scientific & Industrial Research.

Dated this 18th day of Septemper, 1961.

MGIPC—L—104 Patent 62—1-12-62—100.

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74684, 26th December 1960./25th Paus 1882 (Saka).

(Accepted 19th May 1962.)

APPARATUS FOR UNIFORMLY HEATING PARTICULATE MATERIAL

RICE GROWERS ASSOCIATION OF CALIFORNIA, CORPORATION OF THE STATE OF CALIFORNIA, U.S.A., OF SACRAMENTO, CALIFORNIA, UNITED STATES OF AMERICA, MANUFACTURERS.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to an apparatus for continuously heating material composed of discrete particles.

Heretofore it has been customary to heat materials such as rice, coffee, corn, nuts and the like by the batch method; that is, by processing a predetermined quantity of material at a time under controlled conditions of temperature and time. Although such a batch method lends itself to operation under accurately controlled conditions. It is wasteful and inefficient for obvious reasons.

Although it is extremely desirable to employ a "continuous", as opposed to a batch operation in such instances, no satisfactory method or apparatus has heretofore been evolved, presumably because accurate control over the material has not been made possible.

The main object of the present invention is, therefore, the provision of a novel apparatus for permitting continuous heating of material composed of discrete particles without the disadvantages attending the use of the batch method.

Another object of the invention is the provision of an apparatus and method for expanding or "popping" certain granular materials such as rice, corn and the like.

Still another object of the invention is the provision of an apparatus and method for dry heating materials normally requiring fat as a heating medium, such as pop-corn, potato chips, and the like, thereby avoiding raising the caloric content of such materials.

More particularly, the present invention provides the method of uniformly heating material composed of discrete particles, which method comprises conveying said material along a path of travel and simultaneously directing a stream of heated air through said material transversely of said path.

It is also within the purview of this invention to provide apparatus for uniformly heating material composed of discrete particles, said apparatus comprising a generally horizontally extending perforate support, feed means for conveying such material to a first point on said support in a substantially uniform stream, discharge means at a second point on said support spaced from said first point for discharging such material from said support, means for vibrating said support for urging said material from said first point to said second point along a path of travel and means for directing a stream of heated air through said support and through said material thereon during movement of said material along said path.

In a further embodiment of the invention, there is provided apparatus for uniformly heating material composed of discrete particles, which comprises a cylindrical housing arranged with its axis vertical, a horizontal screen extending transversely of said housing and adapted to support material thereon, means for feeding material in a uniform stream onto said screen at a first point adjacent the periphery of the latter, means for removing material from said screen at a second point on the periphery of said screen, means for agitating said screen for progressively moving said material from said first point to said second point, and means for directing a blast of heated air through said screen during said movement.

Other objects, provisions and advantages will be seen in the following specification and in the accompanying drawings wherein:

Figure 1 is a side elevation of the preferred form of apparatus employed in carrying out the invention.

Figure 2 is a greatly enlarged side elevation of a portion of the apparatus of Figure 1 with parts of the same broken away and in section to show internal structure.

Figure 3 is a top plan view of the apparatus of Figure 1.

Figure 4 is a fragmentary cross section of the apparatus showing schematically the path of the heated air relative to the material support.

Figure 5 is a top plan view of a modified form of the invention.

By the present invention the material to be heated or popped is conveyed on a support along a predetermined path of travel and a stream of heated air is directed through said material transversely of the support. In the preferred form of the apparatus the material support is a perforated surface such as a screen and the air is directed upwardly through the screen in a manner to be described.

In order to expose the material to heat for a predetermined length of time it is necessary that a positive control be exercised over the speed of the material along the conveyor to avoid underheating on the one hand and burning on the other hand. This control may be accomplished by use of the apparatus shown in the drawings wherein the numeral 1 generally designates a generally tubular housing having an upper compartment 2 open at its upper end and a lower closed compartment 3 having a bottom 4.

Separating the upper compartment 2 and the lower compartment 3 is a central imperforate plate 6 to the periphery of which is secured an annular screen 7 of relatively fine mesh and which screen extends between said plate 6 and the cylindrical sidewalls of compartment 2.

The upper and lower compartments 2, 3 may be peripherally secured together by a row of bolts 8 so that said compartments constitute a unit.

Extending through the plate 6 and the bottom 4 centrally the same is a cylindrical housing 10 within which is mounted an electric motor 11 arranged with its shaft vertical and coaxial with housing 10. On the upper end of the motor shaft an eccentrically mounted weight 13 is secured and on the lower end of the motor shaft an eccentrically arranged weight 14 is provided (Figure 2).

The above briefly described structure is substantially the same as that disclosed in United States Patent No. 2284671 entitled "Shaking Device", issued to Meinzer on June 2, 1942 and to which reference is made for features of construction and operation not described herein in detail.

As shown in the above cited patent the housing 1 is supported on the upper ends of a plurality of helical compression springs 17, the lower ends of which are secured to a base member generally designated 18. As described in U.S. Patent No. 2284671, rotation of the shaft of motor 11 with its eccentric weights causes vibration of housing 1 with a relatively small applitude in such a manner that material resting on the plate 6 or screen 7 is agitated so as to move in a generally radial direction. By adjusting the eccentricity of the weights 13, 14, a tangential component may be imparted to material in the upper compartment 1 so that the same traverses a generally arcuate path of travel.

In the shaking device disclosed by the reference patent it is contemplated that material to be graded is fed into the upper compartment about centrally of the same and proceeds generally radially outwardly because of the vibration, during which time small particles drop through into the lower compartment 3 and the larger particles are collected adjacent the periphery of the

upper compartment 2. This grading function is not employed by the present invention.

By the present invention advantage is taken of the fact that, although the screen 7 is substantially horizontal, the vibration is such as to cause a progression of the material thereon in a circular path of travel when the weights 13, 14 are properly adjusted to effect such a result.

At a point on the annular support effected by the plate 6 and the screen 7 a radially extending baffle 20 is provided which is secured at one end to the upper end of the inner cylindrical housing 10 and at the other end to the inner side of the sidewalls of compartment 2 (Figure 3).

A feet spout 22 is provided about the compartment 2 along which the material to be heated is conveyed from a hopper 23 to a point above the screen 7 and on one side of the baffle 20. The feeding of material to the screen 7 is preferably established at a uniform rate by any one of many known devices for regulating the flow from hopper 23.

If it is assumed that the direction of rotation of the motor 11 and the disposition of the eccentric weights 13, 14 is such as to cause clockwise progression of the material around screen 7 (Figure 3) such material will ultimately arrive on the opposite side of baffle 20 from which it entered and may be discharged through a discharge spout 25 formed in the sidewall of upper compartment 2 (Figure 1, 3). It is extremely important to note that not only are all particles of the material similarly agitated as they proceed along the circular path of travel but all particles remain on the screen substantially the same length of time.

Alongside the base member 18 is an air blower generally designated 28 which may be driven in any convenient manner by a variable speed electric motor 29 (Figure 3). Adjacent the inlet of blower 28 there are provided one or more burners 30, schematically indicated in Figure 3 for heating the air supplied to blower 28. The discharge pipe 32 (Figure 1) of blower 28 is directed upwardly and is connected by means of a flexible coupling 33 with an air inlet spout 34 provided on the lower compartment 3. The flexible coupling 33, which is preferably of the bellows construction, prevents vibrations of the housing 1 from being transmitted to the blower 28.

The only means of escape of the heated air entering the lower compartment 3 is upwardly through the screen 7 and through the material thereon. It will be apparent that the speed of the blower 28 may be maintained at a predetermined rate and likewise the heat supplied by the burners 30 to the inlet air. Inasmuch as the rate of travel of the material to be heated along the screen 7 may be made uniform as described above, it will be apparent that every particle is subjected to exactly the same length of time. It will further be apparent that the speed of motors 11 and 29 may be varied along with the heat output of burners 30 to obtain any desired result. Thus all of the advantages of batch heating are available with none of the disadvantages.

The heated material discharged from discharge spout 25 may be fed onto a conveyor 36 for further disposition or packaging as desired.

If the material to be heated is composed of particles which increase considerably in size upon being heated, it is preferable to modify the screen so that the same progressively increases in width from the material inlet side to the material outlet side of the baffle 20. Thus in the structure of Figure 5 all elements are the same as above described except that the screen 39 is relatively narrow at the point where the material falls thereon and gradually increases in width to the discharge spout 25. In such a case, the central horizontal plate 40 corresponding to the central plate 6 of Figure 3 is complementarily formed as shown in Figure 5.

By the structure of Figure 5, the density of the material may be made the same at all points along its path of travel thus effecting economy of time and heat.

It will be noted that the vibration of the housing 1 is such that there is little or no tendency for the material to shift radially inwardly of the screen onto the central horizontal plate 6. Inasmuch as the central cylindrical housing 10 extends above the plate 6, the material is prevented from jumping diametrically across the housing and must follow the predetermined path along the screen. If some particles land on the imperforate plate 6 the same are vibrated radially outwardly onto the annular screen as this is a characteristic of the shaker structure disclosed in the reference patent.

It will be apparent that the method herein disclosed for heating material having discrete particles such as rice, coffee or corn, may be visualized and carried out independently of the apparatus disclosed herein although the apparatus above described is preferred.

We claim:

1. Apparatus for uniformly heating material composed of discrete particles, said apparatus comprising a generally horizontally extending perforate support, feed means for conveying such material to a first point on said support in a substantially uniform stream, discharge means at a second point on said support spaced from said first point for discharging such material from said support, means for vibrating said support for urging said material from said first point to said second point along a path of travel and means for directing a stream of heated air through said support and through said material thereon during movement of said material along said path.

2. The apparatus of Claim 1 in which said support comprises a screen, said path of travel is generally circular, means are carried by said screen for defining said circular path of travel, said feed and discharge means are adjacent each other and baffle means separate said feed and discharge means for insuring movement of said materials along said circular path.

3. Apparatus for uniformly heating material composed of discrete particles, which comprises a cylindrical housing arranged with its axis vertical, a horizontal screen extending transversely of said housing and adapted to support material thereon, means for feeding material in a uniform stream onto said screen at a first point adjacent the periphery of the latter, means for removing material from said screen at a second point on the periphery of said screen, means for agitating said screen for progressively moving said material from said first point to said second point, and means for directing a blast of heated air through said screen during said movement.

4. Apparatus for uniformly heating material composed of discrete particles, constructed and adapted to operate substantially as herein described with particular reference to the specific embodiments illustrated in the accompanying drawings.

5. A fungible material having discrete particles, such as rice, coffee, corn, treated in a apparatus according to any of the above claims.

R. HALL,

of REMFRY & SON,

Agent for the Applicants.

Dated this 26th day of December 1960.

M(HTC-LON/8)—103 Patent 62—3-1-63—100.

FIG_1

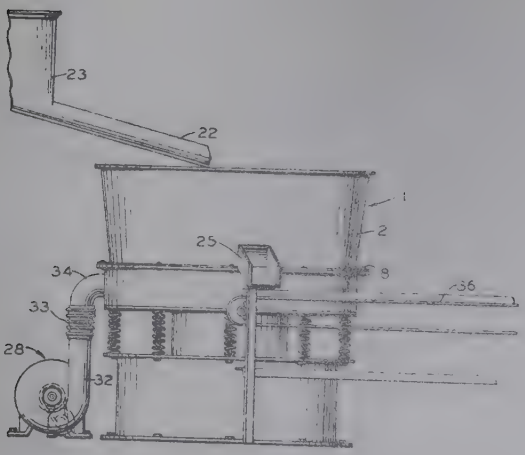
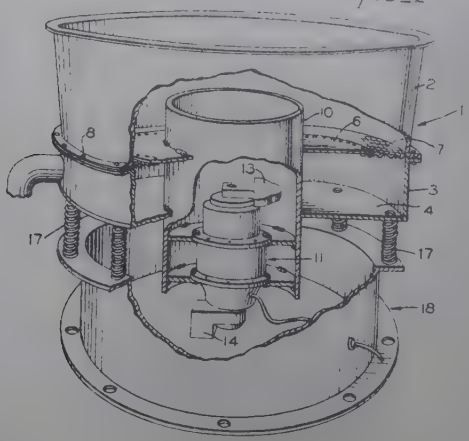


FIG_2



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REG. NO. 2273 E:44—108'63.

PRINTED AT THE SURVEY OF INDIA OFFICES. (P. L. O.).

FIG_3

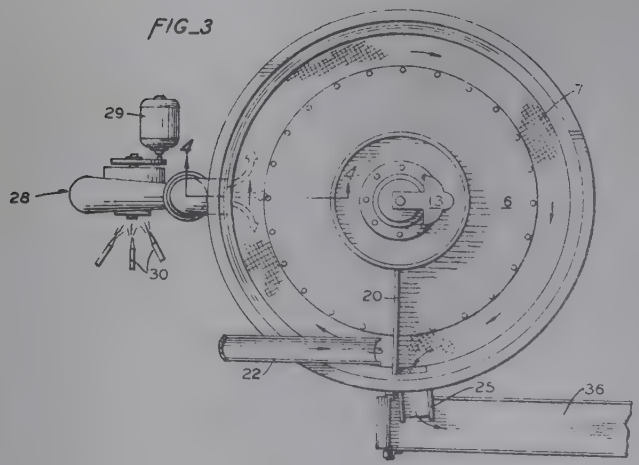


FIG_4

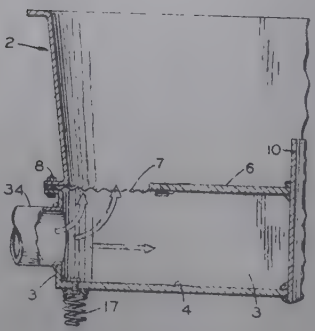
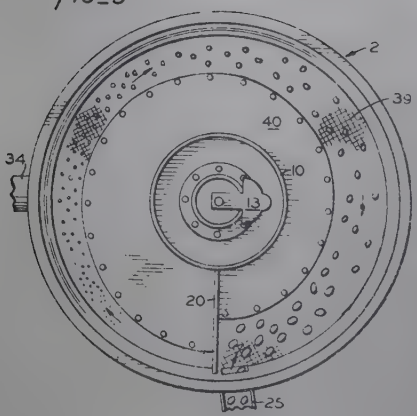


FIG_5



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REG. NO. 2273 E/44—105'63
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For INSPETCION CENTRE

GOVERNMENT OF INDIA : THE PATENT OFFICE 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74685, filed 26th December 1960 (5 Paus 1882 (Saka)) Reciprocity date (United Kingdom) 31st December 1959. (Accepted 11th June 1962.)

"IMPROVEMENTS IN GAIN REGULATING ARRANGEMENTS FOR CARRIES CURRENT TELECOMMUNICATION SYSTEMS"

BRITISH TELECOMMUNICATIONS RESEARCH LIMITED, of Taplow Court, Taplow, Buckinghamshire, England, a Research Company.

The following Specification particularly describes and ascertains the nature of this Invention and the manner in which it is to be performed :—

The present invention relates to electrical signalling systems and is more particularly concerned with telecommunication systems in which intelligence is transmitted by carrier currents over a cable between two terminal stations.

As is well known, if the system comprises a large number of carrier channels so that a comparatively wide frequency band is involved, it is necessary to provide repeater stations at comparatively short intervals along the cable. Moreover for satisfactory commercial working, means must be provided for adjusting the gain of the amplifiers at the various repeater stations in accordance with variations in the transmission characteristics of the cable, so that the end-to-end loss is substantially constant. Regulating devices for this purpose are conveniently classed as dynamic, for instance involving valves or transistors and using a pilot frequency and compatison standard, or static, for instance where thermistors are used to monitor the local cable temperature and adjust the gain of the amplifier accordingly. Dynamic regulators are more complicated and consume more power so that it is usually desirable for them to be located at an attended station where they can receive the necessary maintenonce. Static regulators, on the other hand, seldom give trouble and can therefore be satisfactorily located at an unattended station which may be buried.

It is convenient in many cases to supply the various repeater stations by power transmitted over the cable. It has already been suggested that this power should be supplied on a substantially constant current basis but that slight changes should be made by a dynamic regulator at the feeding termiual station, and that these changes should control static gain regulating networks at the intermediate stations, so giving dynamic regulation with distributed correction for the whole power-fed section. The dynamic regulators may be controlled by pilot current transmitted to the feeding terminal station and applied at a predetermined level.

On an extensive system however, it may not be possible or convenient to feed power from one terminal station only and it may be necessary to feed from both terminal stations with a so-called turn-around point about the middle of the route. With power feeding from both ends however, it is necessary to transmit pilots in both directions and hence to provide dynamic regulators at each end of the line in order to be able to control the two separate feed currents. A little consideration will show that with this arrangement the system will tend to become unstable, since with the use of both-way amplifiers, which is assumed, the pliot current in each direction passes through amplifiers which are controlled by the other pilot current. This confuses the two correcting functions and renders the system unworkable. The expression "both-way amplifier" refers to an arrangement in which the GO and RETURN paths employ different frequency baeds and by the use of suitable high-and low pass filters, a common amplifier may be used for both directions of transmission. The chief object of the invention is to provide an improved arrangement whereby the advantages outlined above are secured but at the same time a satisfactory stability is achieved.

According to the invention there is provided in a gain regulating arrangement for a carrier current telecommunication system including a plurality of repeater stations and employing different frequency bands for the two directions of transmission and common amplifiers in the repeator stations together with power feeding on a substantially constant current basis over the transmission circuit from a plurality of points and having dynamic gain regulators controlled by pilot currents transmitted over the different feed sections which dynamic gain regulators serve to produce variations of the feed current so as to control gain regulating networks in the individual repeater stations, the dynamic gain regulators and pilot generators are located respectively at opposite ends of the power feed section with which they are associated.

The invention will be better appreciated from the following more detailed description of one method of carrying it into effect which is given by way of example only and should be taken in conjunction with the accompanying drawing. This shows diagrammatically one form of the arrangement in which the pilot generators are located at the turn-around point.

It is assumed that a signalling cable extends between the terminal stations T1 and T2 and passes through intermediate repeater stations A1, A2 and A3 of which A3 is somewhere near the middle of the line and serves as the turn-around point. Thus, power feeding to the stations A1, A2 and A3 and any further stastions which may need to be included is from the terminal station T2 where the power source is represented by the battery symbol B1. Similarly, terminal station T2 feeds a number of intermeditate stations assumed to be located between T1 and A3. The arrangement of the both-way amplifier A at station A1 is shown diagrammatically in association with the various filters. It is assumed that a low frequency band is used for transmission in the direction T1-T2 so that signals transmitted from the station T1 pass through the low-pass filter LP1 to the amplifier A and then through the low-pass filter LP2 to the succeeding station. Similarly signals transmitted in the direction T2-T1 in the high frequency band pass through the high-pass filter HP1 to the input to the amplifier A and from the output of the amplifier to the high-pass filter HP2 and thence to terminal station T1. It is assumed that the other intermediate stations are arranged on the same basis.

The division between the two feeding system in station A3 is diagrammatically illustrated by the capacitors C1 and C2 located in the main transmission leads which thus isolate the two direct current supplies. The pilot generator G1 is connected across the signalling leads in the station A3 and produces a frequency f1 which will need to be passed by the high-pass filters HP1 and HP2. This pilot frequency is extracted by the pilot frequency filter PF1 at the terminal station T1 and supplied to the dynamic regulator DR1 which then adjusts the feed current as necessary, for instance as shown diagrammatically in Fig. 1 by means of a slider on the resistor R1. In a similar way the pilot frequency generator G2 at the station A3 produces a frequency f2 which is passed by the low-pass filters it the various intermediate stations and this is extracted at the terminal station g2 by the pilot frequency filter PF2 and operates the dynamic regulator DR2 which accordingly adjusts the feed current from the source represented by the battery

symbol B2 by way of the slider on the resistor R2. It will be seen that with this arrangement each pilot frequency is only effectively transmitted over a single power feed section and consequently there is no question of any amplifier being concontrolled by two pilot frequencies, Accordingly the system has no tendency to instability and operates to give the required adjustments as referred to above.

If one of the pilot frequency generators should become faulty, it is possible to work temporarily with a generator of the same frequency in a terminal station such that pilot transmission will take place in the same direction. Thus, if generator G1 providing frequency f1 should become faulty, the system could still be kept working if a similar generator of frequency f1 were connected up in the terminal station T2. For the reasons pointed out above however, it is not possible to maintain the system in operation if both generators are faulty.

Though present-day repeaters are not unduly sensitive to supply voltage variations, they cannot tolerate large changes without altering their characteristics appreciably. If full advantage is to be taken of the regulating possibilities of the distributed correction scheme, therefore, the feed current may need to vary outside the limits for consistant operation of the amplifier. This point may be taken care of by arranging that the thermistor, which following a known practice, effects the regulation is shunted across the amplifier in series with a Zener diode. This ensures, if the values are suitably chosen, that in spite of the variations of feed current to which the thermistor responds, the voltage across the amplifier and hence the current through it, remains substantially constant. This is shown in the typical station A1 in Fig. 1 where the thermistor heating winding is represented by H and it is connected across the amplifier (including the filters) in series with a Zener diode Z1. The winding H is of comparatively low resistance so that the voltage stabilising effect of the Zener diode is not appreciably impaired. The additional Zener diode Z2, which will have a slightly different characteristic, is provided as a precaution to maintain the stabilising effect in case the heater winding H should become open-circuited. Though this would result in the failure of the gain control in the station in question, it would not put the system out of action and sufficiently satisfactory operation might be possible for some time before the fault was disposed of.

It will be understood that the invention is equally applicable to systems in which one or more intermediate feeding points are employed between the two terminal stations.

WE CLAIM :—

1. A gain regulating arrangement for a carrier current telecommunication system including a plurality of repeater stations and employing different frequency bands for the two directions of transmission and common amplifiers in the repeater stations together with power feeding on a substantially constant current basis over the transmission circuit from a plurality of points and having dynamic gain regulators controlled by pilot currents transmitted over the different feed sections which dynamic gain regulators serve to produce variations of the feed current so as to control gain regulating networks in the individual repeater stations in which the dynamic gain regulators and pilot generators are located respectively at opposite ends of the power feed section with which they are associated.

2. An arrangement as claimed in claim 1 in which the pilot generators for the respective power feed sections are located at the distant ends of the power feed sections with which they are associated.

3. An arrangement as claimed in claim 1 in which in order to feed each amplifier at a constant voltage in spite of variations in feed current the amplifier is shunted by a Zener diode in series with the gain adjusting device.

4. An arrangement as claimed in claim 3 in which the gain adjusting device comprises the heating winding of a thermistor.

5. A gain regulating arrangement substantially as described and illustrated in the accompanying drawing.

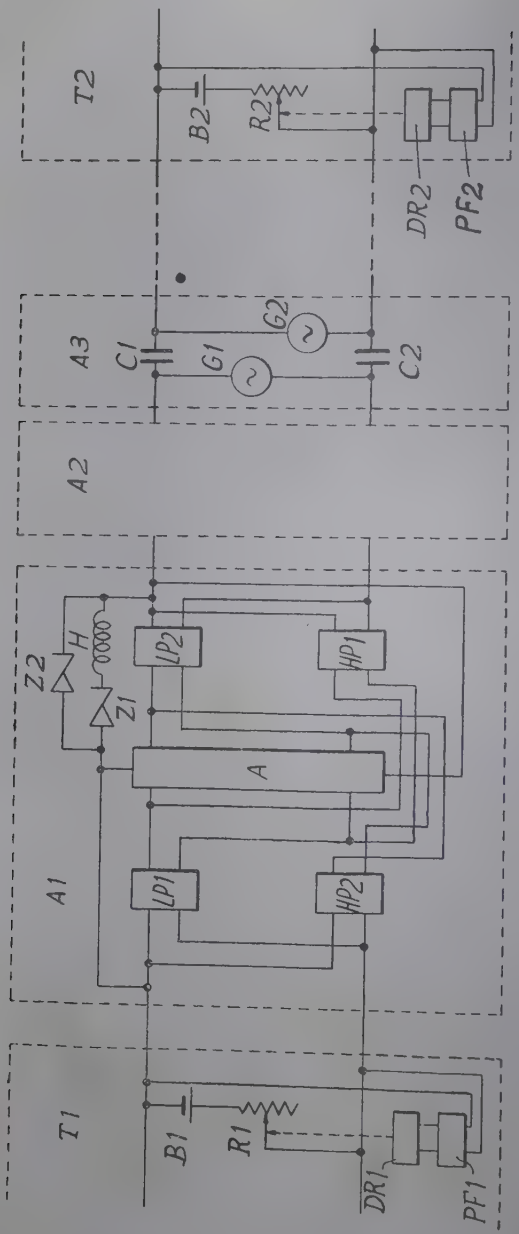
R. HALL
of REMFRY & SON.
Agent for the Applicants.

Dated this 20th day of December 1960.

Printed by The Nelys Printing Works, Calcutta-1.

BRITISH TELECOMMUNICATIONS RESEARCH LTD.
No. 74685 of 1960.

1 Sheet



of REMFRY & SON
Agent for the Applicants

INSPECTION CENTRE

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74686, filed 26th December 1960./5 Paus 1882 (Saka)

(Accepted 26th February 1962).

" DISTRIBUTING VALVE ASSEMBLY FOR PNEUMATIC PERCUSSIVE TOOLS. "

CHICAGO PNEUMATIC TOOL COMPANY, of 6 East 44th Street, New York 17, N.Y., United States of America, Manufacturers, a Corporation duly organized and incorporated under the laws of the State of New Jersey, United States of America.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This invention relates to an improved pneumatic distributing valve assembly for percussive tools of the demolition type, such as pavement breakers and the like.

In the demolition type tool pneumatic pressure fluid is directed by a distributing valve alternately to opposite ends of a piston chamber so as to reciprocate a heavy slide hammer piston relative to an anvil associated with a work steel. It is the purpose of the tool to forcefully and repeatedly pound by means of pneumatic pressure the hammer piston against the anvil to provide effective action of the work steel. In the operation of the tool considerable pneumatic pressure is present in a chamber associated with the distributing valve. Any leakage of pneumatic pressure from this chamber to the return end of the piston chamber during a work stroke of the piston will resist or retard the driving speed of the piston and thereby frustrate or minimize its effects upon the anvil and the associated work steel. It is an object of this invention to provide an improved and efficient pneumatic distributing valve assembly in a percussive tool of the demolition type which avoids such leakage.

At times in the manufacturing of different assemblies of parts for a demolition tool tolerance variations develop which are greater in one run of parts than in another. Where such occur in the housing of the tool or in the casing of the distributing valve assembly there may be leakage of operating pneumatic fluid around the distributing valve assembly to the return end of the piston chamber so as to decrease the efficiency of the tool on a work stroke of the piston,

A further object of this invention is to provide a distributing valve assembly for a percussive tool which is adapted to be effectively assembled in similar chambers of different housings even though such chambers may vary slightly in dimension from one another.

A still further object of the invention is to provide an improved distributing valve assembly in a pneumatic percussive tool of the type mentioned which provides an effective seal between an intake port to the chamber containing the valve assembly and an outlet port of this chamber associated with the return end of the piston chamber.

In accordance with this invention there is provided in a value assembly disposable in a cylindrical pneumatic flow distributing chamber of the housing of a percussive tool having a pneumatically powered piston reciprocable in a piston cylinder wherein the distributing chamber has a pneumatic pressure supply inlet port and has an outlet port connected to the return end of the piston cylinder; a cylindrical casing defining an outer member of the valve assembly having a peripheral inlet groove in communication with the interior of the casing and registrable with the inlet port of the distributing chamber, a peripheral outlet groove in the casing in communication with the interior of the casing and registrable with the outlet port, valve means in the interior of the casing controlling flow of pneumatic pressure fluid from the interior of the casing to the outlet groove, a peripheral seal bing channel in the casing separating the inlet groove from the outlet groove, a compressible resilient seal seated in the channel and projecting in its periphery out of the latter, the casing having an outer diameter less than the diameter of the distributing chamber whereby it is receivable into the latter, the seal ring having an outer diameter greater than that of the distributing chamber, and the seal ring being resilient compressible into the channel to the extent of the difference in the outer diameter of the seal ring relative to the diameter of the distributing chamber, whereby a fluid tight relation is obtainable between the casing and the surrounding wall of the latter chamber upon disposition of the valve assembly into the distributing chamber so that leakage of pressure fluid from the inlet groove around the casing to the outlet groove is blocked.

In the accompanying drawings :

Fig. 1 is a longitudinal section through a pneumatic percussive tool of the demolition type embodying the invention;

Fig. 2 is an enlarged detail of the distributing valve assembly;

Fig. 3 is a further enlarged sectional detail showing the seal ring in its channel in a normal relaxed condition before the distributing valve assembly has been disposed in the housing of the tool;

Fig. 4 is a detail view showing the seal ring fully compressed into its peripheral channel; and

Fig. 5 shows the distributing valve assembly in a housing where there exists a variation from that in Fig. 1 in the clearence between the casing of the valve assembly and the surrounding wall of the housing, and shows an expended condition of the seal ring relative to that shown in Fig. 1 to provide a seal tight relation between the casing and the surrounding wall of the housing.

For a more detailed understanding of the invention reference is now directed to the several figures of the drawing, wherein there is disclosed a pneumatic percussive tool of the demolition type. It includes a housing generally designated 11 comprising a body portian 12 bolted by the usual side tie-bolts, not shown, to a backhead portion 13. The body portion defines a cylindrical piston chamber 14 in which a heavy slide hammer piston 15 reciprocates to forcefully pound an anvil 16 agaiust a work steel, not shown. The bockhead 13 has a recessed inner end which, together with a slightly complementary recessed end in the adjoining body 12, defines a cylindrical pneumatic distribution chamber 17. A trigger operated throttle valve 18 in the housing wall 19 controls flow of pneumatic pressure fluid from a supply inlet 21 to an inner passage 22. The latter opens centrally through the cylindrical wall 23 into chamber 17.

A penumatic flow distributing valve assembly is removably disposed in chamber 17. It comprises a cylindrical container or casing 24 slidably received in chamber 17. Centrally about the periphery of the casing is an annular groove 25 which registers with passage 22. Groove 25 communicates through radial ports 26 with an internal annular groove 27 which opens into a valve chamber 28 centrally of the casing. The left end of the valve chamber is closed by a dead end 29 of the casing. A separable partition disc 31 closes over an open right end of the valve chamber, and separates chamber

Price : TWO RUPEES.

17 from the piston chamber 14. The partition disc abuts about its inner marginal face against a complementary end wall 32 of the casing, and limits about its oppposite marginal area against a recessed internal shoulder 33 of the housing body 12. The dead end 29 of the casing presses against a coned spring washer 34 which abuts the neighboring end wall 35 of chamber 17 and takes up end play or clearance between the valve assembly and the end wall 35.

The valve chamber 28 communicates through a ring of perforation 36 in the partition disc with the rear or driving end 37 of the piston chamber. The valve chamber also communicates through a ring of radial ports 38 in the casing with an annular peripheral outlet groove 39 in the casing. The latter groove or passage is registered with a terminal end of a passage 41 leading through the wall of the body 12 to the forward or return end 42 of the piston chamber.

A shaft 43 integral with the partition disc 32 extends axially and freely through the valve chamber 28, and has a slide fit at its free end in an axial hole 44 of the end wall 29 of the casing. A slide valve 45 shiftable along shaft 43 controls flow of operating pneumatic fluid entering the valve chamber 28, alternately through the perforations 36 and through the peripheral groove 39 to associated ends of the piston chamber.

The slide valve 45 is of T-ring form. It comprises coaxial inner and outer tubular cylinders 46 and 47 integrally connected by an annular web 48. The inner cylinder 46 has a slide fit for longitudinal movement along the shaft 43. The outer cylinder 47 seats in an internal annular groove 49 of the casing upon a pair of annular shoulders 51, 52 between which the inner groove 27 opens into the valve chamber 28. Groove 49 is a little longer in its end to end dimension than the outer valve cylinder 47. Squared end shoulders 53, 54 limit the extent of shifting of the slide valve in one direction or the outer relative to the inner groove 27. When the slide valve is in its left position limited against the left shoulder 53 as in Figs. 1 and 2, a ring of radial ports 55 in the valve cylinder 47 are sealed over by the shoulder 51, and a second ring of radial ports 56 in the valve cylinder 47 are registered with the inner groove 27, whereupon operating pneumatic fluid admitted by the throttle valve 18 to groove 27 flows through ports 56 into the valve chamber to the right side of the valve web 48 and passes through the perforations 36 to the rear end 37 of the piston chamber, thus exerting pressure on the piston and driving the same forwardly. Momentarily before the forward end of the piston pounds the anvil, the rear end of the piston overruns or clears an exhaust vent 10 whereupon the spent driving pneumatic fluid at the rear of the piston exhauste to atmosphere. Residual air in the piston chamber ahead of the piston is trapped and forced by the moving piston through passages 42 and 41 to the valve chamber where it acts upon the web 48 to shift the valve to its right position where it will limit against the shoulder 54. In the latter position of valve, the ring of ports 56 will be sealed over by the shoulder 22 and the ring of ports 55 will be registered with groove 27, whereupon pneumatic flow from the latter will be to the valve chamber 28 at the left of web 48, and through the ports 38 and groove 39 to the return end 42 of the piston chamber to cause return of the piston. Atmosphere air trapped in the piston chamber ahead of the returning piston will pass through the perforations 36 to shift the valve back to the piston shown in Figs. 1 and 2. This shifting or shuttling of the slide valve and reciprocation of the piston continues automatically as long as the throttle valve 18 is held open.

It is obvious from the foregoing manner in which the tool operates that if there is any leakage of pressure air between the casing 24 and the surrounding wall 23 of chamber 17 from the peripheral groove to 25 the peripheral groove 39, the efficiency of the tool on the work stroke of the piston will be impaired. If there is such leakage, pressure air will flow from groove 39 and passage 41 to the forward end 42 of the piston chamber where it will cushion and retard pounding of the piston 15 against the anvil 16. A resilient deformable seal ring 57 seated in an annular peripheral channel 58 of the casing in resiliently pressed relation to the floor 59 of the channel and to the opposed surrounding wall 23 of the housing provides a seal tight relationship between the two which prevents any possibility of leakage of pressure air around the casing from groove 25 to the groove 39 and the associated forward end 42 of the piston chamber.

The seal ring is circular in cross section in its normal relaxed condition externally of the tool, as appears in Fig. 3. It is of soft elastic or live rubber which is readily deformable under pressure, and is adapted to resiliently restore upon relaxing of such pressure. The channel 58 in which the seal ring is seated extends about the periphery of the casing. It is squared in cross section having a flat annular floor 59 and vertical side walls 61. The cross sectional diameter of the seal ring corresponds to the width of the channel, and is slightly greater than the depth of the channel so that the seal ring projects in part out of the channel in its fully relaxed condition, as in Fig. 3. In this fully relaxed condition of the seal ring, the adjacent annular corners 62 of the channel are vacant. As peripheral pressure is applied to the seal ring the latter will, according to the degree of the pressure, be compressed and deformed so as to spread out in its chadnel and fill the vacant side corners 62. The cross sectional diameter of the seal ring relative to the channel 58 is such that the seal ring may be resiliently compressed into the latter and so deformed as to fully occupy the channel substantially leve with the peripheral surface of the casing, as in Fig. 4. When relieved of such pressure the seal ring will resiliently restore to normal.

The structural arrangement of the seal ring and its channel to each other provides various advantages. It enables the valve assembly to be effectively in different housings though these may vary slightly from one another in the diameter of the chamber 17. Such dimensional variations may occur in different manufacturing runs of the housings. In some cases' as in Figs. 1 and 2, the casing 24 of the valve assembly has a slide or close ft in the housing chamber 17, and the seal ring in such cases will be deformed under the pressure of the surrounding wall 23 as to substantially fill the channel. In other cases, as in Fig. 5. because of dimensional variations the fit between the casing 24 and the surrounding wall 23 of the housing is not as close as that in Figs. 1 and 2, as indicated by the clearance 63. In each of the cases exampli-fied in Figs. 1 and 5, the seal ring 57 will nevertheless press resiliently against the floor 59 of its channel and against the opposed surrounding wall 23 of the housing to provide a fluid tight relation between the latter wall and the casing so as to prevent leakage arouund the casing from groove 25 to the groove 39. The dimensional relation of the seal ring 57 to its channel 58, as mentioned above, permits the seal ring according to the pressure thereon to be deformed to a degree wherein it is fully contained in the channel. This avoids overflow any portion of the seal ring laterally upon the periphery of the casing which, if allowed to occur, would prevent a very close slide fit of the valve assembly in a housing.

The extent of such dimensional variations between the housing and casing that may be taken up by the seal ring will be limited substantially to the extent of the normal projection of the seal ring from its channel.

The valve assembly is restrained against longitudinally play in the housing by means of the coned spring washer 34 which is loaded between the dead end 29 of the valve casing and the opposed wall 35 of the housing. The stationary condition given to the valve assembly by the spring washer avoids undesirable slight back and forth movement of the seal ring consequent wear of the latter that might otherwise occur

during the operation of the tool were the spring washer omitted. "Chattering" of the valve assembly is also prevented by this arrangement of the spring washer.

While an embodiment of the invention has been illustrated and described in detail, it is to be expressly understood that the inventian is not limited thereto. Various changes can be made in the design and arrangement of the parts without departing from the spirit and scope of the invention, and it is my intent, therefore, to claim the invention not only as sohwn and described but also in all such forms and modifications thereof as may be reasonably construed to fall within the spirit of the invention and the scope of the appended claims.

WE CLAIM :—

1. In a valve assembly disposable in a cylindrical pneumatic flow distributing chamber of the housing of a percussive tool having a pneumatically powered piston reciprocable in a piston cylinder wherein the distributing chamber has a pneumatic pressure supply inlet port and has an outlet port connected to the return end of the piston cylinder; a cylindrical casing defining an outer member of the valve assembly having a peripheral inlet groove in communication with the interior of the casing and registrable with the inlet port of the distributing chamber, a peripheral outlet groove in the casing in communication with the interior of the casing and registrable with the outlet port, valve means in the interior of the casing controlling flow of pneumatic pressure fluid from the interior of the casing to the outlet groove, a peripheral seal ring channel in the casing separating the groove inlet from the outletgroove, a compressible resilient seal ring seated in the channel and projecting in its periphery out of the latter, the casing having an outer diameter less than the diameter of the distributing chamber whereby it is receivable into the latter, the seal ring having an outer diameter greater than that of the distributing chamber, and the seal ring being resiliently compressible into the channel to the extent of the difference in the outer diameter of the seal ring relative to the diameter of the distributing chamber, whereby a fluid tight relation is obtainable between the casing and the surrounding wall of the latter chamber upon disposition of the valve assembly into the distributing chamber so that leakage of pressure fluid from the inlet groove around the casing to the outlet groove is blocked.

2. In a valve assembly as defined in claim 1, wherein the seal ring channel is squared in cross section and the seal ring is circular in cross section.

3. In a valve assembly as defined in claim 2, wherein the seal ring is of resilient compressible material and, while it is seated in the channel any peripheral deformation thereof is translatable into a corresponding deformation of the inner periphery of the seal ring into the channel.

4. In a valve assembly as defined in claim 2, wherein the cross sectional area of the seal ring corresponds to that of the channel.

5. In a valve assembly as defined in claim 4, wherein the seal ring is formed of elastic rubber material.

6. A valve assembly substantially as described with reference to and as shown in the accompanying drawings.

R. HALL
of REMFRY & SON,
Agent for the Applicants.

Dated this 26th day of December 1960.

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Specification No. 74687, 26th December 1960. 5 Paus 1882 (Sakr). (Accepted 5th June 1962.)

METHOD OF PRODUCING A DEAD BURNED PRODUCT FOR USE AS A REFRACTORY.

HARBISON-WALKER REFRACTORIES COMPANY, A CORPORATION ORGANIZED UNDER THE LAWS OF THE STATE OF PENNSYLVANIA, UNITED STATES OF AMERICA, OF FARMERS BANK BUILDING, PITTSBURGH 22, STATE OF PENNSYLVANIA, UNITED STATES OF AMERICA, MANUFACTURERS.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to the production of dead burned dolomite, dead burned lime, dead burned mixtures of dolomite and lime, and dead burned mixtures of any of the foregoing with free magnesia, in which the resulting products are of very high density, of high purity, and show good resistance to hydration. In particular, the invention is concerned with the production of the foregoing materials for use as refractory materials.

For many years, there have been repeated attempts and many proposals to make use of dolomite and lime as refractory materials. The extremely high melting point of those substances make them very appealing for such purposes, and widespread occurrence make them practical economically. The fact is, however, that commercial success in producing dolomite and lime refractory shapes has been very limited; this is mainly due to their great affinity for moisture, i.e., they hydrate readily with consequent complete breakdown of the bodies into powder. Also, as commonly produced, their density at high purities has been too low for desired uses. Lime particularly has been subject to hydration to a greater degree than dolomite.

Much research has been carried on through the years to discover a means for stabilizing burned lime and dolomite against attack by moisture while retaining their extremely high refractoriness. Numerous chemical additives have been tried but when enough of the chemical had been added to stabilize either of them, the original desirable refractory properties of each were no longer present. Coating the grains and the shaped bodies with oils has also been practiced, but, of course, the cure here is only temporary.

High purity dolomite and lime, after calcination, also normally do not have the high density, and consequent low porosity, desired by the manufacturer and user of refractories. Thus, impurities, *e.g.*, iron oxide, are considered advantageous in the dead burned grain. Although iron oxide acts as a densifying agent, its presence has a deleterious effect on the ability of dolomite and lime to resist the corrosive conditions present in, say, a steel making furnace. Therefore, there has been an apparent need for a dense, high purity dolomite or lime grain that would be resistant to hydration.

For certain applications, it has been found desirable to produce brick composed of varying percentages of lime and magnesia. These brick have proved effective where resistance to slags occurring in steel making processes is of paramount importance. The slags present in the open hearth of oxygen converter are of a complex character, and the reactions between these slags and the brick linings are manifold and far from completely understood. Brick of a varying composition of magnesia and lime have been successfully tested in these applications. Brick of high purity magnesia have shown good resistance to attack by the slags and fumes normally encountered. Nevertheless, it has been found that the presence of some lime in these bodies inhibits the penetration of slag, and thereby further retards the corrosion of the brick.

Brick of this type have heretofore been produced from grains of high purity magnesia and lime or dolomite, which are sized and blended in proportions to yield the desired final composition. The mix is then moulded into brick or other shapes. Since strength, resistance to corrosion and refractoriness are improved with increased density, it is evident that such products can be improved and their usefulness enhanced by forming them from mixes of materials that are extremely dense.

It is, therefore, a primary object of this invention to provide a method of producing dead burned lime, dead burned dolomite, dead burned mixtures of lime and dolomite and dead burned mixtures of magnesia and any of the foregoing, of high purity, high density, and resistance to hydration that is simple, inexpensive, easily practiced with standard equipment, and results in dead burned grain adapted for use in making refractories for high temperature uses.

Other objects will appear from the following specification. It is well known in the refractory art that strength, resistance to corrosion, and refractoriness of a body are improved with increased density. The present invention provides a method for producing an extremely dense grain of the compositions demanded for selected very high temperature service applications.

Briefly, in accordance with the present invention, high purity calcined dolomite, calcined lime, mixtures of calcined lime and calcined dolomite, or mixtures of caustic calcined magnesia and any of the foregoing are briquetted without water or binders under extremely high pressure, and the resulting briquettes are fed into a firing chamber where they are dead burned at high temperatures. The combination of these steps results in such an increase of the density of the grain, over prior practices, as to yield as a final result dead burned dolomite grain of about 3·25 grams per cubic centimeter, dead burned lime grain of about 3·1 grams per cubic centimeter and dead burned MgO-CaO grain ranging from about 3·25 to 3·35 grams per cubic centimeter depending upon the composition of the product. The maximum density of dolomite is about 3·46 and that of lime about 3·34. Accordingly, it is evident that the invention provides grain approaching ideal density.

We have found that the briquetting step under very high pressure is essential and critical in producing grain of maximum density, approaching theoretical, as there is a limit to the amount of densification that can be accomplished in the mere burning of these materials. We have also found that an extremely high dead burning temperature is essential to the production of briquettes possessing the density and hydration resistance desired and which characterize the invention. Thus, temperatures of at least 3400°F are required and up to 4200°F and even higher are necessary to dead burn the briquetted calcined materials to maximum density and resistance to hydration. The higher temperatures of 4000° to 4200° or 4300°F are generally used with compositions having a substantial magnesia content.

In carrying out our process, calcined dolomite or lime, or mixtures of them, of very high purity are used. As to materials, limestone is the source of the lime in the practice of the invention. The limestone is to be of such purity that when calcined the CaO will be at least about 95 per cent, and preferably higher, to obtain the high density desired. As to dolomite, essentially pure dolomites, *i.e.*, $CaCO_3.MgCO_3$, are available that are very low in impurities, and such rocks with not over about 1, or at most 2, per cent impurities are necessary in the practice of the invention. Such purities are exemplified by the following examples.

The limestone and raw dolomite are calcined at a temperature to convert them to calcined products with not over about 2 per cent, preferably not over 1 per cent, ignition loss. Generally, this is accomplished at temperatures from, say, 1600° to 2200°F.

The caustic calcined magnesia of high purity used in the invention is generally the result of calcining magnesium hydroxide precipitated from seawater or other brines, and normally analyzing at least 95 per cent MgO. A suitable calcine can be achieved by calcining in a multiple hearth roaster at 1700° to 2200°F, but any method of burning at those temperatures can be adopted, as long as a product having an ignition loss of not over 1·0 per cent is obtained.

The calcines or their progenitor ores may be crushed or ground to desired particle size, depending on,

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for instance, their character and the calcining conditions, for the dead burned compresses, or briquettes, must be crushed and grain sized in any event to prepare the final refractory shapes or mixes made from them.

The calcined materials, or mixtures of them, are dry pressed or compacted into shaped by briquetting rolls, under extremely high pressure, for example to yield almond-shaped briquettes about 1·5" long, ¾" wide, and ½" thick. No water, temporary or chemical bond is used for these briquettes. The absence of water is, of course, particularly desirable where, as here, the materials are normally extremely prone to hydration which can cause swelling. Pressures of at least 20,000 psi, and preferably higher, are necessary in order to insure high density grain of the final product. Further densification may be achieved by subjecting the compressed bodies to at least one further pressing operation, under similar pressures. However, a single pass through the briquetting rolls has been found to give a body having a density of about 2·0 grams|cc and of such strength that very few broken chips result. These chips are normally screened off and are recycled to the feed to the briquetting rolls in the interest of economy. This briquetting is normally carried out at room temperature although pressing at elevated temperature, such as up to 600°F and higher, has proved very satisfactory. The pressing at elevated temperatures is thought to remove any water mechanically retained by the material thus giving a somewhat denser briquette. Moreover, hot pressing seems to provide a stronger briquette, and therefore would be used to achieve the highest density and strength.

The briquettes are passed to a firing chamber, e.g., a rotary or vertical kiln, where they are dead burned at very high temperatures, suitably at temperatures over 3400°F.

The following examples of our process.

Example I

Calcined dolomite, analyzing about 99 per cent. CaO.MgO on an ignition-free basis and all passing a 10-mesh Tyler screen, was fed to briquetting rolls which produced almond-shaped briquettes measuring about 1·5×¾×½". The material was fed to the press at room temperature. A pressure of 30,000 psi was exerted on the rolls and briquettes having a density of 2·0 grams|cc were produced. No bonding agent, water or pressing aid was added to the material, yet the bodies produced were of such strength that breakage and dusting were extremely limited. The number of fines and chips recovered after screening was so small that they were not recirculated to the feed to the briquetting rolls, although for reasons of economy this can be done.

The briquettes were then conveyed to a vertical kiln operated at temperatures ranging from 3500° to 4000°F in the burning zone. The total time the briquettes were in the kiln was about two hours, about one-half hour of which was spent in the firing zone. When discharged, the briquettes had shrunk to a bulk density of 3·25 grams|cc and a porosity of about 6 per cent.

These briquettes were not only of high density but exhibited a good degree of hydration resistance. One explanation for this property is believed to be that the extremely high density accompanied by very low porosity, limits the number of points at which hydration can begin. It has been found that these briquettes can be stored for periods of over two months with no special protection.

Example II

Calcined lime, analyzing about 96 per cent CaO on an ignition-free basis, and all finer than ¼ inch, was given the same treatment as that described about in Example I. Briquettes having a density of about 1·8 grams|cc were produced by a single pass through the briquetting rolls operating under 30,000 psi. Burning these briquettes at between 3700°F and 4000°F resulted in a bulk density of about 3·1 grams|cc and a porosity of about 7 per cent. These bodies also showed remarkable resistance to hydration in that they have been stored for as long as one month with no special protection.

Example III

Calcined lime, analyzing about 96 per cent CaO on an ignition-free basis and all finer than ¼ inch, was blended in an amount about 10 per cent by weight with caustic calcined magnesia produced in a multiple hearth calciner, analyzing about 96 per cent MgO on an ignition-free basis and all passing a 65 mesh Tyler screen. This mix was fed at room temperature to briquetting rolls which produced almond-shaped briquettes, averaging about 1·5 × ¾ × ½ inches. The briquetting rolls were operated under a pressure of 30,000 p.s.i. and briquettes having a density of about 2·0 grams|cc were produced after a single pass through the rolls. No water, chemical bonding agent, or pressing aid was incorporated in the mix, yet the bodies were of such strength that breakage and dusting were practically non-existent.

The briquettes were conveyed to a burning chamber which in this case was a vertical kiln. The kiln was operated at temperatures ranging from 3500° to 4200°F in the burning zone. The briquettes were in the kiln for about two hours, about one-half hour of which was spent in the firing zone. When discharged, the briquettes had shrunk to a bulk density of 3·30 grams|cc and had a porosity of about 6 per cent.

Example IV

Calcined dolomite, analyzing about 99 per cent CaO.MgO on an ignition-free basis and all passing a 10 mesh Tyler screen, was mixed in an amount about 50 per cent. by weight with caustic calcined magnesia analyzing about 96 per cent. MgO on an ignition-free basis and all passing a 65 mesh Tyler screen. A grain of about 70 per cent. MgO and 30 per cent. CaO was desired. This mix was given the same treatment as that described in Example III. Briquettes having a density of about 2·0 grams|cc were produced after a single pass through the rolls operating under 40,000 psi. Briquettes having a bulk density of 3·25 and a porosity of about 6 per cent. resulted from burning between 3500° to 4000°F.

Examples III and IV show that high purity grain of compositions of magnesia and lime, in which the magnesia forms the major component, can be manufactured through our process which exhibits the high density so necessary in the production of refractories. We have found that the high density, with consequent low porosity, of these briquettes appears to lend resistance to hydration to the bodies. The explanation for this increased resistance to hydration is not fully understood, but as stated above, it is believed that the high density, accompanied by very low porisity, limits the number of points at which hydration can begin. These magnesia containing briquettes have been stored without deleterious effect for periods of over four months with no special protection.

From the foregoing data and discussion, it is evident that the present invention constitutes a unique and effective manner of providing very dense CaO or MgO.CaO grain of particular usefulness in the refractory arts. The composition of the grain, can range from essentially CaO to mixed compositions of MgO.CaO, have a CaO content from 5 weight per cent. upwardly and a magnesia content of up to 95 weight per cent. Where mixed compositions are produced as by adding magnesia to lime or dolomite and producing grain as in this invention, it is preferred that the MgO analysis of the final product exceed about 50 weight per cent. and preferably is at least 60 to 65 weight per cent. of the total. It may be noted that the grain obtained upon use of mixtures of magnesia and lime or dolomite, result in substantially homogeneous grain, and such materials are of greater usefulness in preparing brick or other shapes, than is a mere mechanical mixture of the same analysis.

While the briquetting and burning steps of the invention as set forth hereinbefore are of critical significance in obtaining the dense grain with low porosity, some modification can be made in some of the other steps. For example, in place of providing raw materials for the briquetting rolls, we have found that a mixture of caustic calcined dolomite or limestone with wet magnesium hydroxide can be treated in a hearth-type calcining furnace to provide the requisite calcine of each. The product is obtained intimately admixed

Where it is desired to avoid a double burning to obtain the lime or dolomite caustic calcine, an admixture of crude limestone or dolomite with magnesium hydroxide can be made and subjected to caustic calcining conditions in a hearth furnace.

It will be understood that grain of compositions other than those of the examples can readily be produced by our invention. The burning of the briquettes at the high temperatures employed gives a homogeneous grain, thereby assuring uniformity of composition throughout the brick produced therefrom.

The chemical analyses of the lime, dolomite, and magnesia used in the foregoing examples were:

	Dolomite	Lime	Magnesia
SiO	0.14%	1.59%	1.6%
Al_2O_3	0.25	0.80	0.5
Fe_2O_3	0.09	0.26	0.5
CaO	57.45	95.70	1.1
MgO	41.54	0.91	96.3
Ign. Loss	0.51	0.70	

We claim:

1. The method of producing a dead burned product adapted for use as a refractory and comprising calcined dolomite and/or calcined lime and/or caustic calcined magnesia, said method comprising the steps of mixing the components, briquetting the same without water or binder under extremely high pressure on the order of 20,000 psi., and dead burning the resulting briquettes at high temperatures on the order of 3400 to 4200°F.

2. The method of producing a dead burned product adapted for use as a refractory, comprising the steps of dry forming into small compressed bodies under a pressure of at least 20,000 psi. a composition containing about 5 to 100 per cent CaO and the remainder MgO, where the components of said composition are of high purity calcined lime and/or high purity calcined dolomite, and/or caustic calcined magnesia, and passing said bodies to a furnace and heating them to a temperature to produce a dead burned product of high density.

3. The method as claimed in Claim 2, wherein said bodies are heated at a temperature of about 3400 to 4200°F.

4. The method of producing a dead burned product adapted for use as a refractory, comprising the steps of calcining a mixture comprising magnesium hydroxide and high purity dolomite and/or limestone at a temperature of about 1600° to 2200°F., forming the dry calcined material into small compressed bodies under a pressure of at least 20,000 psi., and passing the compressed bodies to a kiln and heating them to a temperature of about 3400° ot 4200°F. and thereby converting the compressed material to a dead burned condition of high density.

5. The method according to Claim 4, wherein the mixture comprises dolomite and magnesia, the magnesia content being sufficient to provide an MgO content of the resulting grain of at least 50 weight per cent.

6. The method as claimed in any one of the preceding claims, wherein the components in the mixture are calcined to an ignition loss not over about 2 per cent.

7. The method as claimed in any one of the preceding claims, wherein said lime is of at least about 98 per cent. purity, and said dolomite is essentially $CaCO_3.MgCO_3$.

8. The method as claimed in any one of the preceding claims, wherein said briquettes or bodies before being heated are re-pressed at least once under said pressure.

9. The method as claimed in any one of the preceding claims, wherein said calcined materials are at a temperature of at least about 600°F. while being compressed.

10. The method of producing a dead burned product adapted for use as a refractory comprising the steps of calcining at least one high purity material consisting of dolomite and/or limestone to an ignition loss not over about 2 per cent., forming the dry calcined material into small compressed bodies under a pressure of at least 20,000 psi., repressing the bodies at least once under said pressure, recycling for compression at least a portion of any broken parts of said bodies, and passing the compressed bodies to a rotary kiln and heating them to a temperature of about 3400° to 4000°F. and 4000°F. and thereby converting the compressed material to a dead burned condition of high density.

11. The method of producing a dead burned product adapted for use as a refractory substantially as described.

R. HALL,

of REMFRY & SON,

Agent for the Applicants.

Dated this 26th day of December 1960.

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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.
Specification No. 74588, 26th December 1960, 5th Paus 1882 (Saka). (Accepted 7th April 1962.)

IMPROVEMENT IN THE PRODUCTION OF ACETYLENE AND ETHYLENE BY PYROLISIS OF HYDROCARBONS.

MONTECATINI SOCIETA GENERALE PER L'INDUSTRIA MINERARIA E CHIMICA, OF 18 VIA FILIPPO TURATI, MILAN, ITALY, AN ITALIAN COMPANY.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

Many methods are already known for the production of acetylene and olefins by pyrolisis of hydrocarbons in a gas-flow at high temperature, but said procedures have been developed up to to-day by working under a pressure very near to the atmospheric pressure, because it was thought that the equilibrium of the reaction which promotes the formation of acetylene was hindered by the increasing pressure

On the contrary we have now found that when the pyrolisis of hydrocarbons is carried out under suitable conditions, yields of acetylene and olefins which are substantially equal to those obtainable under atmospheric pressure, even if the pressure is raised up to 10 atm. and over.

As the gases produced by the reaction have to be successively compressed in order to separate acetylene and ethylene the pyrolisis of hydrocarbons under pressure allows a very remarkable economy both in plant costs and power consumption over the pyrolisis processes operating at atmospheric pressure.

The present invention provides another interesting advantage in that the water cooling of the gases leaving the furnace allows the recovery of a remarkable amount of heat at a temperature higher than 150°C which can be used to cover the heat requirement of the plant whereby a remarkable saving of steam is achieved.

We have found that in order to obtain satisfactory acetylene and ethylene yields by pyrolisis of a light paraffin base gasoline at a pressure of 10 ata (absolute atmospheres) it is necessary that its flow rate be higher than 800 kg/hr/dm³ of reaction chamber capacity.

When pyrolysis pressure is increased or lowered it is necessary to increase or lower, accordingly, the hourly flow rate of the gasoline.

This is an outstanding advantage of the process according to the present invention because when the pressure is increased in a suitable manner it is possible to realize pyrolisis furnaces having a productive capacity of several tens of tons/day of acetylene and olefins. The gasoline should be pre-heated, before being introduced into the furnace, to the highest temperature permitted by its heat stability and for this purpose it is advisable to mix the evaporated gasoline with steam before introducing it into the superheater

The high temperature gas stream destined to effect the pyrolysis of the gasoline is produced by combustion in the presence of oxygen, of a portion of the residual gas produced in the very plant, after separation of acetylene and ethylene. In order to attain a high thermal yield, it is necessary to provide a complete combustion of the hydrocarbon using gas to oxygen ratios very near to the stoichiometric values, while however, in order to avoid too high temperatures, it is necessary to add a remarkable amount of steam in the combustion chamber.

The steam is easily separated, from the gases leaving the furnace, by condensation, so that it does not hinder the operations necessary to separate the acetylene and ethylene; however it affects the cost of the products appreciably.

The present invention provides a rational method of supplying the steam necessary to the gases by utilizing the heat available in the reaction products.

The accompanying drawing illustrates operation of the plant.

The furnace essentially consists of a cylindrical vertical stainless steel chamber 6 the cooling of which is ensured by evaporating the water contained in an external coaxial jacket.

It is advantageous to keep the vapour pressure comparatively high to avoid excessive heat losses in the combustion chamber and in any case the vapour pressure should be higher than the pressure at which the hydrocarbon is injected into the furnace.

The oxygen and the fuel-gas coming from compressors 1 and 2 are forwarded into the saturation columns 3 and 4 and after pre-heating in 5 they are introduced into the combustion chamber 6.

The fuel-gas may be replaced in part by a corresponding amount of gasoline coming from pump 19. The gasoline to be pyrolyzed is injected into the furnace through the nozzle 7 and 9.

In the reaction zone 8, thanks to the elevated temperature, the formation of acetylene prevails, whilst in the zone 10, where the temperature goes down to 800°C, the formation of olefins prevails.

Finally, the reaction products are quenched with water sprayed by nozzles 11.

The hot water that is collected at the bottom, is conveyed into the column 4 by means of pump 15 in order to saturate the fuel-gas with moisture; the vapour-gas ratio is easily adjusted by varying the water flow-rate.

The gases leaving the furnace firstly pass through the heat exchanger 13 where there is pre-heated the water needed to moisten the oxygen in column 3 and to cover the heat requirement of the plant; then they are cooled in the refrigerator 16 in which together with the steam, the heavier fractions of the hydrocarbons produced are condensed; they separate in the decanter 17 and are utilized as fuels; finally the gases leaving 14 are treated to obtain acetylene and ethylene.

The process affords considerable flexibility and allows to vary within a quite large range the acetylene to ethylene ratio in accordance with the programs of industrial utilization.

We claim:-

1. A process for the production of acetylene and ethylene by pyrolisis of hydrocarbons in a stream of hot gases and steam, characterized in that the steam is supplied to the combustible gas and to the oxygen destined for the combustion, by saturation with hot water heated by the heat of the reaction products.

2. A process for the production of acetylene and ethylene by pyrolisis of hydrocarbons in a stream of hot gases and steam according to Claim 1, characterized in that the operation is carried out at a pressure higher than 3 at., preferably between 10 and 20 at.

3. A process for the production of acetylene and ethylene by pyrolisis of hydrocarbons according to Claim 2, characterized in that the furnace is constituted by a metallic chamber provided with an external jacket cooled by means of the production of vapour at a pressure higher than 10 at.

4. A process according to any of the preceding claims characterized in that in order to avoid the scaling of the heat exchangers steam is added to the gasoline vapour to be pyrolyzed before super-heating it.

W. F. DEPENNING
OF CANTWELL & CO.
Agent for the Applicants.

Dated this 26th day of December 1960.

Price : TWO RUPEES.

MGIP Santh—SL—34 Patent62—12-2-63—100

Montecatini Societa Generale Per L'Industria Mineraria E Chimica.

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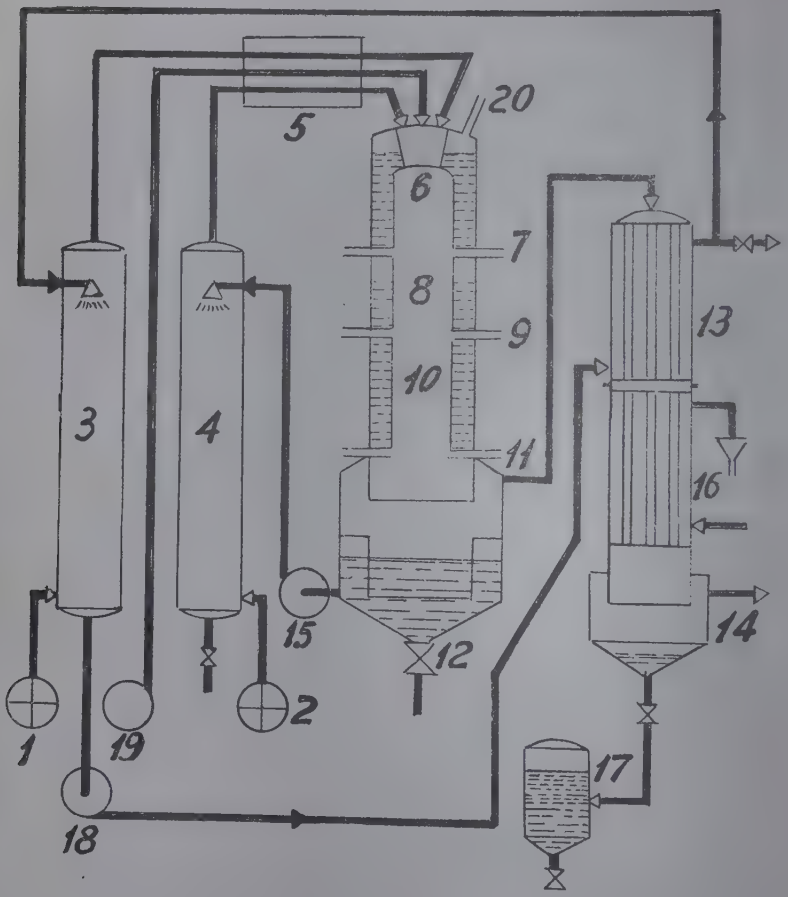

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REG. NO. 2273 E/44—108'52.

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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.
Specification No. 74689, 26th December 1960, 5th Paus 1882 (Saka).
(Accepted 22nd June 1962.)

IMPROVEMENTS IN UREA MANUFACTURE.

MONTECATINI SOCIETA GENERALE PER L'INDUSTRIA MINERARIA E CHIMICA, OF 18 VIA FILIPPO TURATI, MILAN, ITALY, AN ITALIAN COMPANY.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

The industrial processes for the synthesis of urea are all based on the reaction between carbon dioxide and ammonia.

It is known that said reaction is favoured by increasing temperature and pressure for instace when the two reactants in stoichiometric amounts are subted to a pressure of 200 atm at 180·C, only 45% of them is converted to urear, the remainder remaining as carbamate.

On the contrary, by raising the temperature to 210°C. and pressure to 270 atm, a conversion of over 50% may be reached.

The advantages deriving from increasing of pressure are, however, diminished by the higher energy consumption which is necessary to compress the reactants and particularly to pump the unreacted carbamate back into the autoclave.

The present invention provides a method of reducing remarkably the energy consumption necessary for the production of urea as compared with the methods used up to date.

It is known that carbon dioxide is separated from the hydrogen produced from liquid or gaseous hydrocarbons by absorption in water under pressure or in alkaline solutions.

The former method requires an energy consumption of about 300 Kwh per ton of carbon dioxide requiring also a sensible loss of hydrogen; by the latter method the energy consumption is reduced to 40 Kwh/m³, but to regenerate the alkaline solution about 1 ton of steam per ton of CO_2 is needed.

In the two cases considered, the carbon dioxide has to be subsequently compressed to the pressure required for the synthesis of urea.

Instead according to the present invention the carbon dioxide destined for the production of urea, is separated from the hydrogen at a pressure of 300 atm., at which pressure the ammonia synthesis is carried out by cooling at low temperature and then it is conveyed, together with the liquid ammonia, without any further energy consumption, to a reactor for the production of urea, operating at a pressure by little lower than 300 atm.

The accompanying drawing diagrammatically illustrates the process.

From the partial combustion of a fuel oil with oxygen, after the CO conversion, a gas containing about 2/3 hydrogen and 1/3 CO_2 is obtained; said gas is compressed by means of the compressor 1 to 300 atm and, after passing through the heat exchanger 2, it is cooled in the cooler 3 to the temperature of 50°C by means of a refrigerating engine 4. About 80% of the carbon dioxide present in the gas is separated as a liquid in the reservoir 5; the hydrogen is subsequently purified completely from CO_2 and CO in plant 6 and, after addition of nitrogen coming from 7, is introduced into the ammonia synthesis circuit 8.

The carbon dioxide separated by cooling is widely enough to convert all the ammonia produced into urea, and by recovering conveniently the frigories in the exchanger 2, the energy consumption required to condensate the carbon dioxide is reduced to only about 1/10 of the amount which would be needed to eliminate it by washing with water under pressure.

Both carbon dioxide and liquid ammonia coming from reservoires 5 and 9 respectively, are conveyed in the proportions needed for the urea synthesis, by means ofthe automatic flow governor 14, firstly to the heat exchanger 10, then under a pressure of 270 atm to the autoclave 11.

Since the reaction in the autoclave is not quantitative, it is necessary to separate the urea from the carbamate in the apparatus 20 and to recycle the carbamate into the autoclave.

The discharge of carbamate and urea solution from the autoclave has been carried out heretofore by dissipating entirely the energy of the liquid leaving at high pressure and at high temperature, by means of valves which necessarily suffer rapid wear.

The waste energy of the solution from the autoclave is exploited, according to the present invention, to compress the carbamate again into the autoclave.

The device consists essentially of a couple of coaxial cylinders 18, in which the pistons are made rigid with each other by means of the rod 19.

The urea and carbamate solution leaving the autoclave passes through the heat exchanger 16 to lower its temperature from 210·C. to 140·C. which preheating the ammonia and the carbon dioxide prior to their introduction into the autoclave; by said expedient the chemical corrosion of the apparatus is avoided by reducing the chemical aggressiveness of the urea.

By means of the distributor 16, the solution discharged from the autoclave is alternately forwarded to the outer ends of the cylinders A and D while the opposite sides B and C act as a common hydraulic pump, sucking the carbamate from the condenser 22. through the valves *e* and *f*, and compressing it into the autoclave.

The arrows of the drawing show the circulation of the liquid during the movement of the piston from the top to the bottom; the force acting upon the face A of the piston is higher than that acting upon the face B because of the pressence of rod 19 and the difference provides the thrust necessary for the operation of the device.

At the end of the stroke the distributor 17 reverses the circulation of the liquid. As the volume of the urea and carbamate solution leaving the autoclave is much higher than the volume of the carbamate injected by means of the pump, it is necessary to discharge the difference into the circuit after the pump by means of the vaive 12.

The separation of the carbamate from the urea and its total recycling to the autoclave are carried out in two steps; about 75% of the carbamate is first separated in the apparatus 20 and subsequently the remainder 25% is separated in the apparatus 24.

The solution leaving the distributor 16 under a pressure of 15 to 30 atm is forwarded, after a rapid heating in the evaporator 13, to the separator 20, where the evaporating carbamate is condensed again at a temperature of from 80· to 100·C. in the lower section 22 in order to prevent the salt from crystallizing.

The inert gases contained in the ammonia and carbon dioxide are washed in the small tower 21 with a small amount of water introduced through pipe 34 to recover the carbamate vapors.

The urea solution leaving the separator 20 is subjected to a treatment analogous to the preceding one, but at a pressure of from 0·5 to 1·5 atm, in the distilling apparatus 23, and in the apparatus 24.

The carbamate solution is forwarded by means of pump 27 to the condenser 22 and from here is introduced into the autoclave 11 with energy recovery by means of the pump. The urea solution which is concentrated under vacuum up to 99% in the distilling apparatus 28, is forwarded by means of the pump 30 to a granulation tower 33. Since the urea solution contains some g/l of ammonia, the vapor leaving the separator 15, is subjected to a fractional condensation in the column 31 to recover the ammonia as a concentrated solution. The column is operated under vacuum by means of a vacuum pump 32 and with a barometric discharge (of ammonia free excess condensate) at 35.

Said solution is recycled by means of the pump 29 into the condenser 24 allowing thus to get a conversion yield of ammonia into urea very close to 100%.

We claim:

1. A process for making urea from ammonia and carbon dioxide, using a mixture containing carbon dioxide and hydrogen as a starting material, characterized in that the carbon dioxide is separated from the hydrogen at ammonia synthesis pressure by cooling down to low temperature and is subsequently introduced without further compression into the urea synthesis reactor, whilst the remaining hydrogen is lead to an ammonia synthesis.

2. A process according to Claim 1, characterized in that the energy of the urea and carbamate solution coming from the autoclave, is utilized by means of a pump with double-effect coaxial cylinders for recompressing the unreacted carbamate into the autoclave.

3. A process according to Claim 1 or 2, characterized in that the unreacted carbamate is separated from the urea by means of two stages, each of which comprises a distillation and a condensation, the distillation and condensation of the first stage being effected at a pressure of less than 30 atm., but preferably at more than 15 atm., and the distillation of and condensation of the second stage being effected at a pressure of less than 5 atm., but preferably at more than 0.5 atm., the pressure of the first stage being however at any rate higher than that of the second stage.

4. A process according to any of Claims 1 to 3, characterized in that the vapours leaving the last concentrating stage of the urea solution, are condensed fractionately in order to recover the ammonia contained therein.

B. DEPENNING,
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Agent for the Applicants.

Dated this 28th day of December 1960.

MOP South—SL—106 Patent/62—27-6-63—100.

200°C. The dimensions of the product were: Outside diameter 1·365 in., inside diameter 1·000 in.

Example III

Manufacture of Pipe from a High Density Polyethylene Resin

Pipe of good quality was made from a high density polyethylene having a density (measured after conditioning a shock-cooled sample at 100°C. for 1 hour) of 0·94 gm|cc and having a melt index measured by ASTM D-1238 of about 0·5. The apparatus was as described in the preceding examples. Extrusion conditions were: Barrel temperature 180-190°C., crosshead and die were maintained at a temperature in the range of 190°-200°C. and pipe was formed at the rate of 18½ in|minute.

Example IV

Fabrication of biaxially oriented pipe from polyoxymethylene resin

The polymer employed in this example was a polyoxymethylene resin characterized by a number average molecular weight greater than 15,000 and a rate constant for thermal degradation at 222°C. of less than 1% by weight per minute, as described in U. S. Patent No. 2,768,994.

Pipe stock was extruded having an internal diameter of 1·185" and an outer diameter of 1·615", and a wall thickness of 0·215" using the method described hereinabove. The billet was passed through a rolling mill substantially as described hereinabove and as shown in Figures 3, 4 and 5 of the appended drawings. The flared section of the mandrel was 1·593" in axial length and had a diameter of 1·180" at the smaller end and an outer diameter of 2·195" at the larger end. The conical surface of the mandrel had an included angle of 31° for a distance of 0·485", beginning at the smaller end of the conical surface, and an included angle of 40° for the rest of the flare, thereby conforming closely to a concave surface of radius 6", which was determined to be ideal for the rolls of the mill. The axes were offset by ⅛" from the center line of the mill, thus providing assistance to the feeding device. The mandrel was cooled internally with a rapid stream of water between 5-10 gallons|minute maintained at a temperature of approximately 60°C. The mandrel was adjusted to the desired gap by a screw adjustment on the tension bar supporting the flared head. The head was screwed in until it was in contact with the rolls, then retracted to give a minimum axial gap of 0·110". The stock was fed into the mill at a rate of 6½" per minute at a head speed of 144 rpm. The resultant pipe had a smooth, glossy inner and outer surface, had an outside diameter of 2·378", an inside diameter of 2·135" and a wall thickness of 0·120". The deformation ratios thus achieved were: axial 1·11; hoop 1·61. In Table I, the properties of the resultant pipe are compared to those of pipe extruded in the same fashion to comparable dimensions, but not oriented by the rolling technique described above.

Table I

Properties of Extruded and of Biaxially Oriented Polyoxymethylene Pipe

Property		Extruded Axial	Extruded Hoop	Oriented Axial	Oriented Hoop
Yield Strength (psi)		9600	8100	8500	14,000
Ultimate Strength (psi)					
% Elongtion		30	20	60	50
Impact strength by weigh drop ft, lbs., room temperature		27		67	
Law temperature brittleness		−28°C.		−58°C.	
Brust strength 45°C., in water	10 hours	4100		5600	
	100 hours	3050		4300	
	1000 hours	2250		3400	

Example V

Biaxially oriented pipe from 66 nylon (polyhexamethylene-adipamide)

Pipe stock was fabricated from a high molecular weight extrusion grade polyhexamethylene adipamide. The mandrel was fed with cooling water at 60°C., and oil was supplied to the outside of the pipe stock as it was fed through the rolling mill. The experimental details were otherwise similar to the previous example. The dimensions of the initial billet or pipe stock were 1·170" internal diameter, 1·580" outside diameter and wall thickness 0·205". After expansion over the mandrel, the pipe had an internal diameter of 2·140", an outer diameter of 2·370" and a wall thickness of 0·115". The mandrel gap had been set as described hereinabove to a distance of 0·115". A feed of 10"| minute with 156 rpm of rolling head was employed. The deformation ratios were, therefore, 1·13 in the longitudinal direction and 1·63 in the hoop direction.

In Table II, nylon pipe manufactured according to these directions and nylon pipe extruded to comparable dimensions but not rolled were found to have the following properties:

Table II

Properties of Biaxially Oriented Pipe of Polyhexamethylene adipamide

Test		Extruded Axial	Extruded Hoop	Oriented Axial	Oriented Hoop
Yield Strength psi		6000		5500	15,000
Burst Strength psi, 45°C., in water	10 hours	3200		5500	
	100 hours	2700		5300	
	1000 hours	2400		5000	
Impact Strength by Weight Drop Test ft. lbs.) 0°C.		70		126	
Low Temperature Brittleness °C		−34		−71	

Example VI

Biaxially oriented polypropylene pipe

Polypropylene having a melt index of 0·39 as measured by ASTM method D-1238-52-T was extruded in the form of a billet of internal diameter 0·955", 1·344" outside diameter and 0·195" wall thickness. The pipe stock was rolled on a mandrel having a flare with a smaller diameter of 0·950", a larger diameter of 1·650", the length of the flares being 1·100", the mandrel was cooled internally by a stream of oil. Some oil was also added to the external surface of the polypropylene during its passage through the rolls. The final dimensions of the product were: outer diameter 1·825", internal diameter 1·610" and hence wall thickness of 0·107". The deformation ratio was thus 1·24 in the longitudinal direction and 1·46 in the hoop direction. The yield strength of unoriented pipe comparable in dimensions was found to be 4,300 psi in the axial direction and 3,150 psi in the hoop direction, a small amount of orientation being introduced by the extrusion. After orientation, the axial yield strength was found to remain at about 4,000 psi, but the hoop yield strength increased to 5,800 psi. The low temperature brittleness was found to be +18°C. in the unoriented sample, but in the oriented material was found to be −16°C.

We claim:

1. An apparatus for the manufacture of pipe from thermoplastic material that comprises a crosshead, a heated die attached to the crosshead, the heated die having an outlet substantially defining the outer surface of the pipe, a mandrel substantially defining the inner surface of the pipe, said mandrel being disposed axialy within the crosshead and the die, and means to supply molten thermoplastic material under pressure to the crosshead, characterized in that the mandrel comprises (1) a heated section, and (2) a cooled section abutting the heated section and continuing within the crosshead and the die at least to a plane defining the face of the die, and there are provided means for heating the heated section of the mandrel, means for cooling the cooled section of the mandrel, means for cooling the pipe, and means for withdrawing the pipe from the die.

2. An apparatus according to Claim 1 characterized in that there is provided means for mechanically de-

forming the pipe to produce biaxial molecular orientation.

3. An apparatus according to Claim 1 or 2 characterized in that the cooled section of the mandrel is in contact with, but thermally isolated from the heated section of the mandrel by an air gap over the greater part of the cross-section, the heated section contacting the cooled section only at a knife edge about the periphery of the sections.

4. An apparatus according to any of Claims 1-3 characterized in that the cooled section of the mandrel is cooled by a fluid coolant.

5. An apparatus according to any of Claims 1-4 characterized in that the means for cooling the pipe comprises fluid coolant supplied to the interior of the pipe as the pipe leaves the mandrel.

6. An apparatus according to any of Claims 1-5 characterized in that the means for heating the heated section of the mandrel comprises an electrical resistance heater.

7. An apparatus according to any of Claims 1-6 characterized in that there is provided means for exterior forming of the pipe that comprises passing the pipe through a snugly fitting former of polytetrafluoroethylene.

8. An apparatus according to any of Claims 1-7 characterized in that there is provided means for exterior cooling of said pipe comprising contact with a fluid coolant upon emergence from said die.

9. An apparatus according to any of Claims 1-8 characterized in that the heated die is heated by an electrical tape heater.

10. An apparatus according to any of Claims 1-9 characterized in that the means for mechanically deforming the pipe comprises a mandrel that flares outwardly in the direction of feed of the pipe, a plurality of conical rolls rotating substantially epicyclicly about the flare of the mandrel, means to drive the rolls, means to cool the mandrel and means to feed the pipe over the flare of the mandrel in the direction of increasing diameter.

11. An apparatus according to Claim 10 characterized in that the mandrel of the rolling mill is supported by a rod extending from the center of the heated die of the extrusion apparatus.

12. An apparatus according to Claims 10 or 11 characterized in that the means for cooling the mandrel comprises passing the coolant from the internal extrusion core through an annular passageway formed between the mandrel supporting rod and the extrudate then through and around the flare in the mandrel and out through the finished product.

13. An apparatus according to any of Claims 10-12 characterized in that the included angle of the flare is from 20° to 70°.

14. An apparatus according to any of Claims 10-13 characterized in that the axes of the conical rolls are laterally displaced so that they do not intersect on the axis of the mill but pass by the principal axis so that the least distance from the principal axis is 1/10 to 1/4 of the diameter of the pipe.

15. An apparatus according to any of Claims 10-14 characterized in that there is provided means to drive the conical rolls substantially epicyclicly about the flare.

16. An apparatus according to any of Claims 10-15 characterized in that the gap between the rollers and the flare in the mandrel linearly decreases at an angle of about 3°.

17. An apparatus according to any of Claims 10-16 characterized in that the mandrel consists of an outer shell having substantially the form of a truncated cone that merges into a cylindrical section.

18. An apparatus according to any of Claims 1-17 substantially as hereinbefore described.

19. A process for the manufacture of pipe from thermoplastic material that comprises supplying molten thermoplastic material to a crosshead under pressure and forming and cooling said molten thermoplastic material characterized in that it comprises continuously forming a solid skin within said molten thermoplastic material under pressure about a cooled rigid support that substantially defines the interior of said pipe withdrawing said skin from the pressure zone as said skin is formed, forming the molten thermoplastic material about said skin to the form of the outer surface of said pipe, and cooling said pipe until said pipe has solidified.

20. A process according to Claim 19 characterized in that the pipe is biaxially oriented by mechanical deformation.

21. A process according to Claims 19-20 characterized in that the interior of said pipe is cooled by fluid coolant supplied to the interior of the pipe as the pipe leaves the forming die.

22. A process according to any of Claims 19-21 characterized in that the exterior of the pipe is cooled by contact with a fluid coolant upon emergence from the forming die.

23. A process according to any of Claims 19-22 characterized in that the skin is about 10 to 20 mils in thickness at the point where the extrudate leaves the die.

24. A process according to any of Claims 19-23 characterized in that the outer surface of the pipe is formed by passing through a snugly fitting former of polytetrafluoroethylene resin.

25. A process according to any of Claims 19-24 characterized in that the diameter of the pipe is increased while simultaneously reducing the wall thickness by rolling, and the temperature of the pipe is maintained lower than the melting point of the thermoplastic.

26. A process according to any of Claims 19-25 that comprises urging the pipe over a flared mandrel while simultaneously reducing the thickness of the pipe by the compressive rolling action of a plurality of conical rolls rotating substantially epicyclicly about the pipe as it passes over the mandrel.

27. A process according to any of Claims 19-26 characterized in that the pipe is passed through two or more rolling mills in succession.

28. A process according to any of Claims 19-27 characterized in that the reduction of wall thickness per pass of each roller is between 0·1% and 10% of the predetermined total reduction.

29. A process according to any of Claims 19-28 characterized in that the mandrel is cooled to a temperature in the range between 60°C. and a temperature 50°C. below the crystalline melting point of the thermoplastic polymer.

30. A process for the manufacture of biaxially oriented pipe of a thermoplastic material that comprises forming thick-walled tubular pipe stock from thermoplastic material characterized in that the diameter of the stock is increased while simultaneously reducing the wall thickness by rolling, and the temperature of the pipe is maintained lower than the melting point of the thermoplastic.

31. A process according to any of Claims 19-30 characterized in that the diameter is increased while simultaneously reducing the wall thickness by the compressive rolling action of a plurality of conical rolls rotating substantially epicyclicly about the stock as it passes over the mandrel.

32. A process substantially as described in any of the foregoing Examples.

33. A process according to any of Claims 19-32 substantially as hereinbefore described.

34. A process according to any of Claims 19-33 characterized in that the thermoplastic material is a polyoxymethylene.

35. A process according to any of Claims 19-32 characterized in that the thermoplastic material is polypropylene.

36. A process according to any of Claims 19-33 characterized in that the thermoplastic material is a polyamide.

R. HALL

for REMFRY & SON,

Agent for the Applicants.

Dated this 22nd day of May 1961.

Malvern Printing Co., Ltd.—166 Patent/62—27-6-63—100.

Montecatini Societa Generale Per L'Industria Mineraria E Chimica.

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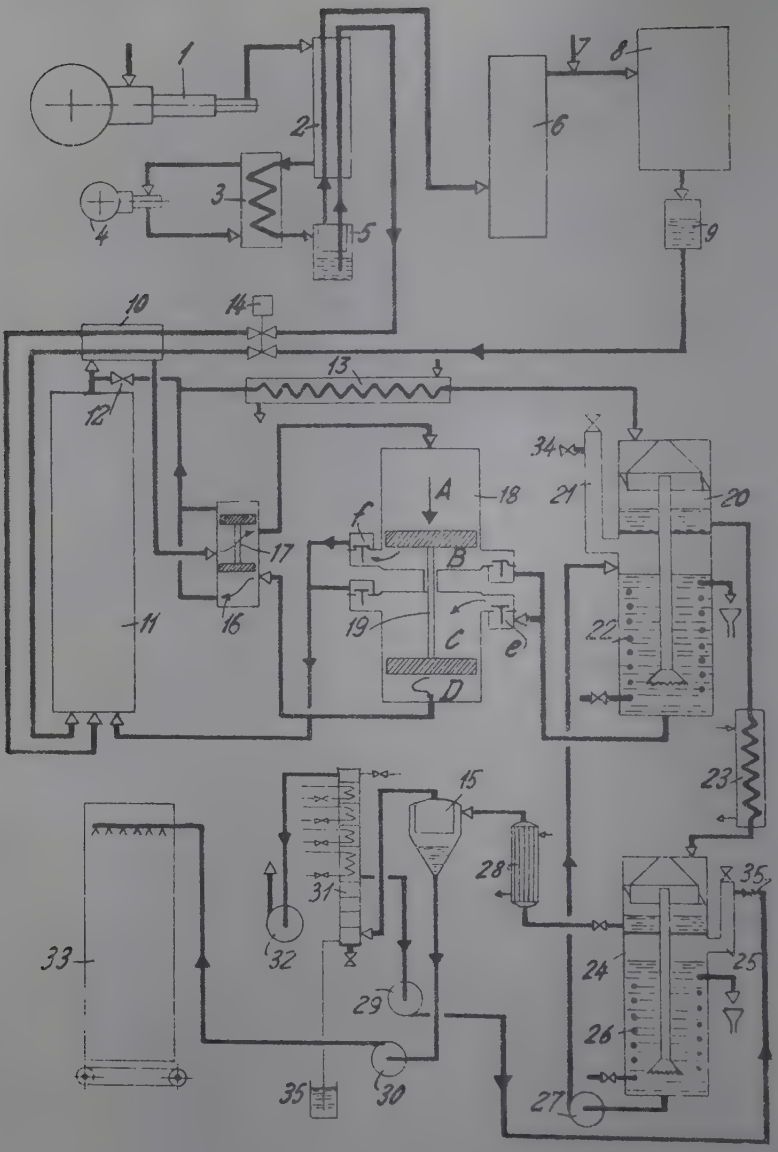

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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74690, filed 27th December 1960.
(Accepted on 11th January 1962).

"IMPROVEMENTS IN MEANS FOR STRAIGHTENING CONTINUOUSLY ACCRUING ROD MATERIAL."

CONCAST AKTIENGESELLSCHAFT, of Stockerstrasse 33, Zurich 2, Switzerland, a Swiss Company.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

Straightening machines are employed for straightening continuously accruing material, particularly rolled stock. The material is guided round, between positively driven rollers arranged above and below it, in an upward and downward direction, out of the direction of motion, until with an appropriate adjustment of the straightening rollers, it finally runs out of the straightening machine in a straight line.

If however the rod of material, issuing from a vertical continuous-casting plant, is to be straightened after being deflected into a horizontal plane, a series of difficulties arise, which with straightening machines can only be overcome with difficulty and in part with a comparatively heavy expenditure.

The rod issuing from a continuous casting plant usually has a speed of advance ranging from about 0.5 to 6 metres per minute, and is known to be very sensitive to distortions. On the other hand this rod material may be of comparatively large cross-sectional areas, which would involve a very costly straightening machine. The introduction of the rod into the set of straightening rollers of straightening machines also gives rise to serious difficulties, since the straightening rollers thereof are very difficult of access.

The problem of the invention is to provide straightening apparatus which obviates the disadvantages of the straightening machines usually employed for straightening rod material, and will not be very expensive, but will be robust and reliable in operation.

As a solution of this problem, apparatus is provided which consists of a line, roller bed conveying the material, and, on the side of the material remote from the line-roller bed, of rotatable rollers, adjustable independently of one another, each adapted to co-operate with one live roller of the conveying bed.

According to a further feature of the invention, the rollers adjustable independently of one another are adjusted hydraulically, by way of rocking levers or the like for example, relatively to the live rollers allocated to the latter. All the rollers of the apparatus are preferably cooled, for the purpose of the better removal of heat. The adjustable rollers, or at least one of them, may be driven in synchronism with the live rollers. Guiding bars are provided between the adjustable rollers for the reliable guidance of the rod.

One constructional example of the invention is illustrated in the accompanying drawings in which:

Figure 1 shows the apparatus in front elevation in section on the line I-I in Figure 2;

Figure 2 shows the same apparatus in side elevation in the working position; and

Figure 3 shows the same apparatus in side elevation in section on the line III-III in Figure 1.

By 1 is denoted line, roller conveying bed, which forms a continuation of an inclined slideway 2, which supplies to the straightening means a rod 3, coming from a vertical continuous, casting plant not shown in the drawings.

The rollers of the conveying-roller bed 1 are driven by a motor 5*a* through a clutch 5*b*, by means of chains 4*a* passing around chain wheels 4 and a deflecting roller 5, and over a tensioning roller 6. On both sides of the conveying-roller bed 1 are arranged parts of a frame 7, on which shafts 8 and 9 are journalled above the conveying-roller bed 1. Levers 10, 10*a*, 11 and 11*a* are mounted rotationally fast upon the shafts 8 and 9. On the free ends of the levers 10*a* and 11*a*, rollers 12 are rotatably mounted. The free ends of the levers 10 and 11 are pivotally connected with piston rods 14 of pistons not shown in the drawing, guided in cylinders 15 and 16. The cylinders 15 and 16 are rockable about pivots 17. Between the shafts 8 and 9 is arranged a guiding bar 18 for guiding the in-coming rod 3.

When the rod 3, coming from a vertical continuous-casting plant not shown in the drawings is supplied to the straightening-roll bed by way of the inclined slideway 2, the levers 10, 10*a*, 11 and 11*a* with the rollers 12 are deflected as shown in Figure 3, and the leading end of the rod 3 runs into the straightening apparatus. When the leading end of the rod 3 has passed the roller 12 rotatably mounted on the lever 11*a* on the entry side, the roller 12 is pressed against the rod 3 by supplying fluid to the cylinder 16 and thereby rocking the levers 11 and 11*a* about the shaft 9. The rod 3 runs at first in the direction 3', represented by a chain-dotted line in Figure 3. When the leading end of the rod 3 reaches the roller 12 rotatably mounted on the lever 10*a* on the outlet side, the cylinder 15 is supplied with fluid, and, by the rocking of the levers 10 and 10*a* the roller 12 on the lever 10*a* is likewise pressed against the rod 3, so that this roller is now advanced in to alignment with the plane of conveyance of the roller bed 1, as shown in Figure 2.

The rollers 12 may if desired be driven in synchroniam with the rollers 1, in order to exert a better straightening action upon the rod 3. After the rod 3 has passed through the straightening means, the rollers 12 are moved back into their initial position by rocking out the levers 10, 10*a*, 11 and 11*a*.

The construction of the adjusting mechanism for the rollers 12 is only to be regarded as a constructional example; solutions are also possible in which the rocking levers 10, 10*a* and 11*a* may be omitted.

WE CLAIM :—

1. Apparatus for straightening continuously accruing rods, with rollers arranged above and below the moving material, characterised by the feature that a line-roller bed conveying the material is provided, and at the side of the material remote from the roller bed are arranged rotatable rollers adjustable independently of one another, and each adapted to co-operate with one of the rollers of the line-roller bed.

2. Straightening apparatus as claimed in claim 1, characterized by the feature that the rollers adjustable independently of one another are adjustable hydraulically, for instance by means of rocking levers.

3. Straightening apparatus as claimed in claim 1, characterised by the feature that means are provided for cooling the rollers.

Price : TWO RUPEES

4. Straightening apparatus as claimed in claim 2, characterised by the feature that one or both of the adjustable rollers are driven in synchronism with the roller-bed rollers.

5. Straightening apparatus as claimed in claim 1, characterised by the feature that guiding bars are provided between the adjustable rollers.

S. K. Datta.
of T. P. DATTA & SONS.
Agent for the Applicants.

Dated this 27th day of December 1960.

Printed by The Nelys Printing Works, Calcutta-1.

Applicant - Concast Aktiengesellschaft

No. of Sheet 1

No. 7690 of 1960

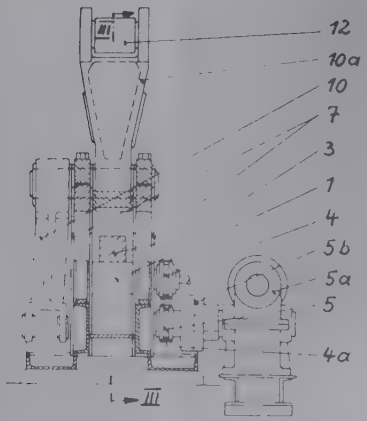

Fig. 1

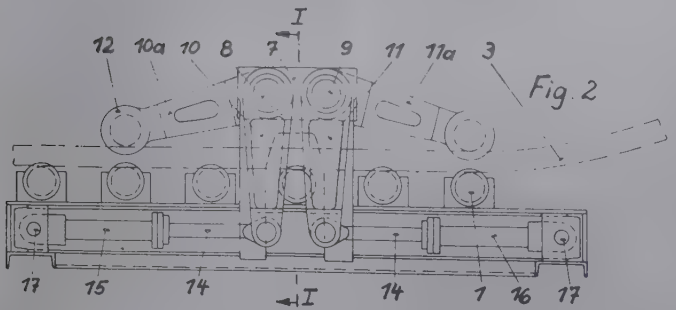

Fig. 2

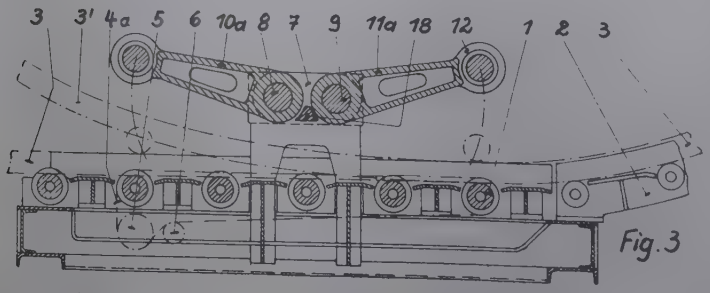

Fig. 3

Signature

of T. P. Sutton & Son,

Agent for the Applicants

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.
Specification No. 74691, dated the 27th December 1960 (6 Paus 1882, Saka). Accepted 18th May 1962.

PROCESS FOR THE DEHYDROGENATION OF HYDROCARBONS.

SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., A NETHERLANDS RESEARCH COMPANY, AT 30, CAREL VAN BYLANDTLAAN, THE HAGUE, THE NETHERLANDS.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

The invention relates to a process for the dehydrogenation of hydrocarbons by means of iodine.

The reactions of hydrocarbons with iodine, in which the hydrcarbons are dehydrogenated and iodine is converted into hydrogen iodide are known. In these reactions alkenes, alkadienes and alkapolyenes are formed from alkanes, and alkadienes and alkapolyenes are formed from alkenes. In addition the splitting off of hydrogen may be accompanied by the formation of bonds between carbon atoms. Thus, for example, a cyclic or an aromatic hydrocarbon may be formed from an acyclic hydrocarbon, and a dicyclic hydrocarbon from a monocyclic hydrocarbon having an acyclic group in the molecule. Two radicals formed by splitting off of hydrogen may combine to form a new molecule. Examples of the said reactions are the preparation of butenes and butadiene from n-butane ; of butadiene from butenes ; of isobutene from isobutane ; of pentadienes from pentanes and pentenes ; benzene from n-hexane ; toluene from n-heptane ; naphthalene from butylcyclohexane ; diallyl from propene ; dibenzyl and stilbene from toluene. In some cases other reactions occur at the same time as dehydrogenation, e.g., isomerizations, dealkylations, and exchange of hydrogen atoms or alkyl groups between various hydrocarbons.

One of the considerations which led to the invention is that in the reaction of hydrocarbon with iodine it should be regarded as important to shift the equilibrium as far as possible to the side of dehydrogenated hydrocarbon and hydrogen iodide.

In its widest sense the invention provides a process for the dehydrogenation of hydrocarbons by reacting these hydrocarbons with iodine, characterized in that the reaction takes place in the presence of substances binding hydrogen iodide in the form of inorganic iodides.

This binding of hydrogen iodide is to be understood as comprising both the binding of hydrogen iodide present in the reaction mixture and the binding of hydrogen and iodine without the two latter having first formed hydrogen iodide together.

A second advantage of the binding of hydrogen iodide is that when the temperature falls after the dehydrogenation the reaction cannot proceed in the reverse direction, viz. with reformation of hydrogen-rich hydrocarbon and iodine, and moreover the hydrogen iodide cannot enter into any undesirable subsequent reactions. To prevent the reaction in the reverse direction and undesirable subsequent reactions rapid cooling is applied in the known processes, which can therefore be omitted in the process according to the invention.

The hydrogen iodide-binding materials are usually metal compounds, e.g., oxides, hydroxides or carbonates. As a result of reacting with hydrogen iodide these compounds are converted into metal iodides. Use is preferably made of metal compounds which yield iodides from which iodine can be recovered by treating with oxygen or oxygen-containing gases in a separate operation.

Other hydrogen iodide-binding materials may also be used, however, for instance, ammonia.

Very good results were obtained when iodine is reacted with hydrocarbons in the presence of oxides or hydroxides of one or more of the following metals : calcium, nickel, zinc, cadmium, indium, tin and the rare earth metals. These metals yield iodides which can be very readily converted into oxides by means of oxygen or oxygen-containing gases. When the oxygen treatment is accompanied or followed by a water vapour treatment, the hydroxides may, be formed instead of the oxides. In certain cases hydroxides are formed during the hydrogenation by reaction of the oxides with water vapour formed *in situ*.

When butane, iodine and calcium oxide are used as starting materials, reactions take place according to the following equations :

$$C_4H_{10}+I_2+CaO \dashrightarrow C_4H_8+C\ I_2+H_2O$$
$$C_4H_8+I_2+CaO \longrightarrow C_4H_6+CaI_2+H_2O$$

Iodine and calcium oxide are regenerated according to the equation :

$$2CaI_2+O_2 \longrightarrow 2CaO+2I_2$$

Use may also be made of compounds of metals which have more than one valency state, the valency decreasing under the conditions of the dehydrogenation reaction and increasing under the conditions of the regeneration. Examples of such compounds are the oxides of iron, cobalt manganese and copper. When butane, iodine and ferric oxide are used as starting materials the reactions proceeds as follows :

$$3C_4H_{10}+2I_2+Fe_2O_3 \longrightarrow 3C_4H_8+2FeI_2+3H_2O$$
$$3C_4H_8+2I_2+Fe_2O_3 \longrightarrow 3C_4H_6+2FeI_2+3H_2O$$

It may be imagined that HI is first formed by dehydrogenation of the hydrocarbon with the iodine and that this HI is then partly oxidized to I, by Fe_2O_3 FeO also being formed which yields FeI_2 with remaining HI. Hence the iodine is in this case partly regenerated *in situ*. There is a possibility of the remaining some FeO which is not converted into FeI_2.

Fe_2O_3 is regenerated according to the equation :

$$4FeI_2+3O_2 \longrightarrow 2Fe_2O_3+4I_2$$

The oxides which, like Fe_2O_3, also have an oxidizing effect and certain other oxides, may cause undesirable side-reactions, thereby wholly or partly destroying the desired dehydrogenated hydrocarbon. Such side reactions may be suppressed by mixing the metal oxide with alkali metal, alkaline earth metal and/or ammonium compounds, in particular oxides, hydroxides, carbonates and halides of the alkali metals, for example sodium oxide, potassium oxide and potassium iodide.

Metal compounds binding hydrogen, iodide may also be salts which react with hydrogen iodide, with the formation of an acidic oxide, when iodides are formed which by treatment with oxygen and the acidic oxide may be reconverted into the original salts. Examples are the carbonates or bicarbonates of lithium, sodium, potassium and strontium in particular, and also the carbonates or bicarbonates of rubidium, cesium, barium, thallium and germanium. When the starting materials are butane and potassium carbonate the dehydrogenation reactions should proceed according to the following equations :

$$C_4H_{10}+I_2+K_2CO_3 \longrightarrow C_4H_8+2KI+CO_2+H_2O$$
$$C_4H_8+I_2+K_2CO_3 \longrightarrow C_4H_6+2KI+CO_2+H_2O$$

and the regeneration according to :

$$4KI+O_2+2CO_2 \longrightarrow 2K_2CO_3+2I_2$$

Where reference is made hereinbefore to metal oxides, in certain cases metaloxy-iodides may also be used as hydrogen iodide-binding materials instead of these oxides or in addition thereto. On the other hand it is also possible for metaloxy-iodides to be formed instead of metal iodides or in addition thereto in the dehydrogenation reaction.

For bringing together the hydrocarbon to be dehydrogenated, iodine and hydrogen iodide-binding material various orders of mixing may be used. It is possible, for example, first to mix the hydrocarbon with

iodine and to contact the resultant mixture with the hydrogen iodide-binding material either immediately or after a certain degree of dehydrogenation has taken place. Hydrocarbon, iodine and hydrogen iodide-binding material may each be introduced into the reaction mixture either at once or gradually.

As a rule the hydrogen iodide-binding materials, in particular metal oxides, will be present in the reaction mixture in solid form, for example as a fixed or fluidized bed. The process, may, however, also be carried out very well with hydrogen iodide-binding materials in the liquid state, e.g., present in the form of a melt. If desired materials may be added which do not themselves bind hydrogen iodide, but which yield at the temperature prevailing in the reactor a solution or melt with the hydrogen iodide-binding material or materials present. The iodides formed may in some cases also form a melt with the oxides.

If desired, the hydrogen iodide-binding materials may be used together with carriers which are inert per se, such as alumina, magnesia and silica. In such a case the hydrogen iodide-binding material will usually be brought on to the surface of the carrier in a finely divided state. Suitable carriers are porous materials in particular

Oxygen, may, if desired, be incorporated in the mixture in which the dehydrogenation is to take place. This oxygen may contribute to the dehydrogenation and is bound to the hydrogen split off from the hydrocarbon. This hydrogen is probably intermediately bound to iodine. Larger amounts of oxygen, however, cause difficulties.

It is also possible to incorporate substances giving off oxygen into the reaction mixture. Moreover, a related possibility is that in addition to the hydrogen iodide-binding material a compound is present which does not bind hydrogen iodide but only oxidizes it. This compound may be molybdenum oxide, for example. If desired, the mixture of hydrocarbon and iodine may be successfully passed through two reactors one of which contains the oxidizing agent and the other the hydrogen iodide-binding material.

It is advisable to use the hydrogen iodide-binding material in excess of the hydrocarbon to be dehydrogenated and iodine. This hydrocarbon and iodine may be mixed in a stoichiometric ratio or else in such ratios that after completion of the reaction either unconverted hydrocarbon or iodine remains behind. The iodine remaining in such a case may be bound by addition of another hydrocarbon which is partly dehydrogenated as well, preferably one which can itself and also the dehydrogenation product thereof be readily separated from the hydrocarbon to be prepared, for example by making use of the difference in boiling points.

In some cases more hydrogen is abstracted from the hydrocarbon than the hydrogen which in the form of hydrogen iodide is bound to the hydrogen iodide binding material. In the dehydrocyclization of n-hexane with certain metal oxides, e.g., nickel oxide, cobalt oxide, copper oxide, as the hydrogen iodide binding material more benzene is produced than can be calculated from the equation

$$C_6H_{14} + 4I_2 \rightarrow C_6H_6 + 8\ HI.$$

Probably a catalytic effect plays a part. The catalytic factor (*i.e.*, the amount of benzene actually produced divided by the amount calculated from the above equation) may be considerably above, 1 for instance 2 or even higher.

The temperatures at which hydrocarbons are dehydrogenated and iodine is regenerated are usually in the range of from 300°C. to 700°C. usually 400 to 600°C. In certain cases temperatures lower than 300°C., may, however, also lead to favourable results, particularly during the regeneration reaction (for example 150-300°C.). The pressure employed may be atmospheric pressure, although higher or lower pressures also may be used.

The process according to the invention will generally be carried out continuously, although it may also be effected batchwise.

Example I.

Butane was dehydrogenated in a quartz tube 25 cm. long and having a cross-sectional area of 0.9 sq. cm. The tube was vertically arranged in a controllable electric furnace.

The bottom 10 cm. of the tube were packed with Fe_2O_3 impregnated with KI (7.2 g. of Fe_2O_3, 2.8 g. of KI). The mixture was granulated into 0.5-2 mm. pieces. The top of the tube was filled with pieces of procelain.

The temperature in the Fe_2O_3 was 530°C. A mixture consisting of 0.77 litres butane, 2.45 litres nitrogen and 4.4 g. iodine was passed through from the top to the bottom over a period of 50 minutes. This mixture entered the tube at a temperature of 300°C. and was then pretreated in the porcelain packing to 530°C.

From the composition of the gas mixture leaving the bottom of the tube, it was found that 18 per cent. of the butane had been converted into butenes, 29 per cent. into butadiene, 41 per cent. was unconverted, 8 per cent. was cracked, and 4 per cent. was converted into CO, CO_2 and water. No iodine was observed in this gas mixture.

By heating the packing of the bottom part of the tube after completion of this test in an air stream at 600°C. the iodine incorporated therein was entirely recovered.

Example II.

Except for the differences referred to below, this Example is identical with Example I.

Instead of Fe_2O_3 impregnated with KI, pure Fe_2O_3 was used (10 grams). The temperature in the bottom part of the tube averaged 550°C. A mixture of 0.89 litres butane, 2.63 litres nitrogen and 11 grams of iodine was passed through over a period of 1 hour.

43 per cent. of the butane was converted into butenes and 6 per cent. into butadiene. In addition, 19 per cent. was cracked and 13 per cent. converted into CO, CO_2 and water. 19 per cent. was unchanged. No iodine was present in the gas mixture leaving the reactor.

Example III.

The apparatus was the same as in Example I. The tube was packed over a length of 20 cm. with 25 grams of CaO in 0.5-2 mm. pieces.

The temperature in the bottom part of the tube average 520° C. A mixture of 0.93 litres butane, 2.54 litres nitrogen and 16 grams of iodine was passed through the tube from top to bottom over a period of 62 minutes.

The iodine was fully bound to CaI_2 by CaO.

8 per cent. of the butane was converted into butenes and 72 per cent. into butadiene, 15 per cent. was unchanged. 2 per cent. was cracked and 3 per cent. converted into CO, CO_2 and water.

CaO was regenerated as in Example I. The regenerated CaO was used again in the dehydrogenation. In this manner ten cycles were performed with the same material without there being any significant difference in the results.

Example IV.

In this Example 6 grams of CaO supported on 12 grams of carrier were used. As such sintered kieselguhr ("Sil-O-Cel") was used having a particle size of 0.2-0.5 mm.

The temperature in the bottom part of the tube (equipment as in Example I) averaged 515°C. A mixture of 1.13 litres butane, 2.66 litres nitrogen and 11 grams iodine was passed through from top to bottom over a period of 65 minutes.

The iodine was entirely taken up by the CaO.

18 per cent. of the butane was converted into butanes and 26 per cent. into butadiene, 49 per cent. was unchanged, 3 per cent. was cracked and 4 per cent. converted into CO, CO_2 and water.

The regeneration was effected as in Example I.

EXAMPLE V.

The reactor was a quartz tube having a volume of 200 ml. and a length of 25 cm. The reactor was placed in a bath of molten salts of which the temperature could be controlled.

The reactor was packed with 18.1 grams NiO supported on 80.1 grams of pumice stone. The teperature in the reactor was varied from 450°C. to 540°C. in ten successive cycles.

In each cycle 3.8 litres of butane and 58.3 grams of iodine were passed through in 52 minutes (no nitrogen).

In all cycles the iodine was substantially entirely bound. Regeneration was carried out with air at the same temperatures as dehydrogenation.

The results were substantially the same in all cycles.

In the cycle which was carried out at 510°C. 39 per cent. of the butane was converted into butenes and 48 per cent. into butadiene, 9 per cent. remaining unchanged, 2 per cent. being cracked and 2 per cent. destroyed by oxidation.

EXAMPLE VI.

The apparatus was the same as in Example V. The tube was packed with 13 grams of Mn_3O_4 supported on 93 grams of pumice stone. The temperature in the reactor was 515°C. A mixture of 1.4 litres butane, 4.1 litres nitrogen and 24.2 grams iodine were passed through in 9 minutes.

The iodine was entirely bound by the Mn_3O_4.

11 per cent. of the butane was converted into butenes and 51 per cent. into butadiene, 32 per cent. was unchanged, 2 per cent. was cracked and 4 per cent. was converted into tarry products, CO, CO_2 and water.

The regeneration was carried out with air at the same temperature as the dehydrogenation.

EXAMPLE VII.

Normal hexane was converted to benzene in a quartz tube having a cross-sectional area of 1.33 cm^2. The tube was packed with 10 grams of pumice containing 20 per cent. NiO. The temperature in the reactor was 520°C. A mixture containing 11.5 per cent. mol. of n-hexane, 13.5 per cent. mol. of iodine and 75 per cent. mol. of nitrogen was passed through the tube. The contact time was 1.3 sec. and the WHSV (weight hour space velocity) i.e., the amount of hexane, expressed in grams which is passed per hour through the hydrogen iodide binding material divided by the amount (in grams) of hydrogen iodide binding material (present+carrier) was 0.4.

From the composition of the reaction product it was found that 40.4 per cent. of the hexane had been converted into benzene, 48.9 per cent. was unconverted, 4 per cent. had been cracked, 5.7 per cent. converted into CO, CO_2 and water and 1.9 per cent had been converted into tarry materials. The catalytic factor was 1.35.

EXAMPLE VIII.

Except for the differences referred to below, this Example is identical with Example VII. A mixture containing 11.5 per cent. mol. of n-hexane, 13.5 mol. of mol. of iodine, 9.8 per cent. mol. of oxygen and 65.2 per cent. mol. of nitrogen was passed through the reactor at a WHSV of 0.4.

65.4 per cent. of the n-hexane was converted into benzene, 14.3 per cent. was unchanged, 9.8 per cent. was cracked, 8.2 per cent. converted into CO, CO_2 and water and 2.3 per cent. was converted into tarry materials. The catalytic factor was 2.18.

EXAMPLE IX.

This Example is identical with Example VII, except for the differences referred to below. A mixture containing 23 per cent. mol. of n-hexane, 27 per cent. mol. of iodine and 50 per cent. mol. of nitrogen was passed through the tube. The contact time was 2.6 sec. and the WHSV was 0.4.

47.4 per cent. of the n-hexane was converted into benzene, 40.0 per cent. was unchanged, 3.3 per cent. was cracked, 6.9 per cent. converted into CO, CO_2 and water and 2.4 per cent. was converted into tarry materials. The catalytic factor was 1.58.

EXAMPLE X.

This Example is identical with Example VII, except for the differences referred to below. A mixture containing 11.5 per cent. mol. of n-hexane, 13.5 per cent. mol. of iodine and 75 per cent. mol. of nitrogen was passed through the reactor. The contact time was 2.6 sec. and the WHSV was 0.2.

55.3 per cent. of the n-hexane was converted into benzene, 27.5 per cent. was unchanged, 10.0 per cent. was cracked, 5.2 per cent. converted into CO, CO_2 and water and 2.0 per cent. was converted into tarry materials. The catalytic factor was 1.84.

We claim:

1. A process for the dehydrogenation of hydrocarbons by reacting these hydrocarbons with iodine, characterized in that the reaction takes place in the presence of substances binding hydrogen iodide in the form of inorganic iodides.

2. A process as claimed in Claim 1, characterized in that metal compounds are used as hydrogen iodide-binding materials.

3. A process as claimed in Claim 2, characterized in that metal compounds are used which yield iodides from which iodine may be recovered by treatment with oxygen or oxygen-containing gases.

4. A process as claimed in Claim 3, characterized in that the metal compounds used are oxides or hydroxides of one or more of the following metals: calcium, nickel, zinc, cadmium, indium, tin and the rare earth metals.

5. A process as claimed in Claim 3, characterized in that use is made of compounds of metals whose valency is reduced during the conversion into iodides.

6. A process as claimed in any one of Claims 2-5, characterized in that in addition to the metal compounds referred to in the said claims, alkali metal compounds, alkaline earth metal compounds, or ammonium compounds or mixtures thereof are present.

7. A process as claimed in Claim 2, characterized in that the metal compounds used are salts converted during the reaction of hydrocarbon with iodine into metal iodides, with the formation of an acidic oxide, after which the metal iodides are regenerated by treatment with oxygen and the acidic oxide, with re-formation of iodine, to form the first-mentioned salt again.

8. A process as claimed in any one of Claims 1-7, characterized in that iodine is used in a quantity in excess of that which would be required according to the reaction scheme to obtain the desired effect, and that the excess of iodine is removed afterwards by the addition of one or more hydrocarbons from which hydrogen is also removed by the iodine, the latter hydrocarbons and the dehydrogenation product obtained therefrom being physically separated from the desired dehydrogenation product.

9. A process for the dehydrogenation of hydrocarbons by reacting these hydrocarbons with iodine, substantially as described in any of the forgeoing Examples.

R. HALL,

OF REMFRY & SON,

Agent for the Applicants.

Dated this 27th day of December 1960.

M.(I.P.C.)—L (N/8)—103 Patent/62—27-2-63—100.

GOVERNMENT OF INDIA : THE PATENT OFEICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.
Specification No. 74692, 27th December 1960, 6 Paus 1882 (Saka). (Accepted 22nd June 1962.)

IMPROVEMENTS IN OR RELATING TO ELECTRIC CIRCUIT BREAKERS.

THE ENGLISH ELECTRIC COMPANY LIMITED, Electrical and Mechanical Engineers, of English Electric House, Strand, London, W. C. 2, England, a Company registered under British Law.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to electric circuit breakers.

According to the invention in one aspect, a gas blast electric circuit breaker includes two gas blast circuit interrupters arranged for simultaneous operation and having separate contact enclosures which are arranged for permanent communication with a common source of compressed gas and which communicate with the atmosphere through a common exhaust valve, the opening of said exhaust valve causing a blast of gas to flow through the two contact enclosures during opening operation of the circuit breaker. The separating movement of the contacts of the two circuit interrupters at the commencement of an opening operation of the circuit breaker is preferably dependent upon or made in correspondence with the opening of the exhaust valve. The contact enclosures may be tubular insulators projecting one from each side of a common centre section which supports the exhaust valve and also forms the connections to the common source of compressed gas, the gas blast produced during operation of the circuit breaker thus passing outwardly from the centre section to the interrupters and returning inwardly to be exhausted through the exhaust valve. The arrangement is particularly applicable to circuit breakers in which the two interrupters are electrically connected in series as part of two or more serially disposed points of circuit interruption; the two interrupters may then be electrically connected together through the centre section, by which they are also mounted on a suitable support insulator.

According to another feature of the invention, a gas blast electric circuit breaker, particularly though not necessarily a circuit breaker as defined in the next preceding paragraph, includes an exhaust valve which when open connects the interior of a contact enclosure of the circuit breaker with the atmosphere to permit the flow through the enclosure of a blast of compressed gas, a movable valve member of the exhaust valve being arranged for permanent biasing towards its closed position by compressed gas acting on a differential area of the valve member; the valve member may in addition be biased towards its closed position by springs or by its own weight.

According to the invention in another aspect, a gas blast electric circuit breaker includes two or more pairs of interrupting contacts, the movable contacts of the pairs being arranged for simultaneous actuation but having no positive mechanical connection between them, a common valve for controlling a blast of gas through separate contact enclosures for the pairs of contacts and arranged to open at the commencement of an opening operation of the circuit breaker, and means for allowing the said valve to close only after a predetermined total movement of all the movable contacts of the said contact pairs towards their open positions. The preferred embodiment of the invention has two pairs of associated contacts; the said means then includes a lever having two points in its length connected so as to move in correspondence with the respective movement of the movable contacts, and having a third intermediate point connected with closing means for said valve, so as to allow the valve to close after a predetermined movement of said third point. In this embodiment, one arm of the spring loaded toggle forming part of the arrangement defined in the next preceding paragraph may be connected with one of the outer points of the lever to provide the movement corresponding to that of the associated contact.

According to another feature of the invention, an electric circuit breaker includes a power driven contact actuating mechanism and a control member linking the contact actuating mechanism with a remotely situated primary actuating mechanism, the control member being movable between "close" and "trip" positions to initiate corresponding operations of the circuit breaker, and being biased to its "trip" position by a spring acting on the end of the member nearer the contact actuating mechanism. The spring preferably acts to place the control member under tension at least when in its "close" position, in which it may be held by a releasable latch, in the primary actuating mechanism, which then constitutes the circuit breaker tripping control.

The foregoing and other features of the invention will be evident from the following description of a unit of high voltage air blast switchgear, embodying the various features of the invention in their preferred forms. The description refers to the accompanying drawings, in which :

Fig. 1 shows in side elevation the general arrangement of the circuit breaker;

Fig. 2 shows in axial section the internal arrangements of an interrupter unit forming part of the circuit breaker, with the contacts in their closed positions;

Fig. 3 is a view similar to Fig. 2 but representing the condition of the interrupter towards the end of an opening operation thereof;

Fig. 4 is a view of the control mechanism associated with a pair of interrupters;

Fig. 5 is a cross sectional view of part of the control mechanism; and

Figs. 6 and 7 show diagrammatically the linkage by which the control mechanism shown in Figs. 4 and 5 is linked with the primary actuating mechanism in the circuit breaker base.

Fig. 1 of the drawings shows the general arrangement of the circuit breaker. A cylindrical receiver 10 for compressed air carries two hollow vertical insulators 11, each supporting from its top cap 12 a pair of short insulating support arms 13, mounted at an angle to the horizontal and also at an angle to the centre-line of the receiver 10. Each arm 13 supports an interrupter assembly 14, comprising two air-blast interrupter units 15 mounted in opposition by means of a common centre section 16. The interrupters of each pair are connected electrically in series by the centre-section 16, and the pairs of interrupters are also connected in series. The end terminals 17 of the chain of interrupters form the line terminals of the circuit breaker.

The insulators 11, the support arms 13 and the interrupter units 15 are all in internal communication with each other and with the air receiver 10, and are all therefore filled with compressed air. Exhaust valves 18, mounted on the centre section 16 of each interrupter pair, are controlled (by a mechanism hereinafter to be described) so that they open to permit the flow of a blast of air through the interrupters and across their arcing spaces during opening operations of the circuit breaker. The interiors of the insulators 11 and the support arms 13 form wide-bore conduits offering negligible resistance to the flow of compressed air. When an exhaust valve 18 is open, the air blast passes outwardly from the centre section 16 of the interrupter pair to the vicinity of the interrupter contacts, whence it returns, its direction of flow having been reversed, to the centre section and is exhausted to the atmosphere through the open valve.

The air receiver 10 is mounted at earth potential, but since the air flow through the interrupters is controlled solely by the exhaust valves 18, and since the interiors of the support insulators 11 and the support arms 13 form wide-bore conduits for the compressed air flow, the air blast is effective at the interrupter contacts immediately after the initiation of the air blast during a switching operation. The circuit breaker structure can be dynamically balanced with respect to the reaction forces of discharged air.

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The immediate actuating mechanism for the interrupter contacts and for the exhaust valves 18 is housed in the interrupter centre sections 16, and is connected by control rods passing down the support arms 13 and the support insulators 11 to the common control apparatus 19, which is arranged not only for the simultaneous control of all the interrupters of the circuit breaker but also for the simultaneous control of other associated circuit breakers, for example forming the various phases of a three-phase circuit breaker.

The construction of one of the individual interrupter assemblies is shown more clearly in Figs. 2 and 3. The assembly is built up on the casting that forms the centre section 16 of the interrupter pair, and which also houses or supports the control apparatus for the interrupters. The insulators 20 that form the housings of the interrupters are mounted on either side of the centre section 16 by means of flanges 21; further flanges 22 and 23 provide respectively a mounting means for the assembly at the top of the support arm 13, and the connection with the exhaust valve assembly 18.

The fixed contact assembly 24 of each interrupter is supported on the interrupter end plate 25, which also forms one terminal of the interrupter. The fixed contact assembly consists essentially of a generally-tubular main contact 26 solidly bolted to the end cap 25 and formed by a series of longitudinal cuts at its inner end into a series of resilient contact fingers 27, biased inwardly both by their own resilience and by garter springs 28. Within the tube defined by the contact fingers 27 slides an arcing contact 29, provided with a stem 30 that extends into a cylinder 31 and terminates in a piston 32. A spring 33 biases the arcing contact towards engagement with the moving contact.

The moving contact assembly 40 comprises a tubular moving contact member 41, having the movable throat contact 42 at one end and supported by means of radial arms 43 on a central stem 44, which also carries the internal arcing probe 44a of the contact assembly. A fixed sleeve 45 surrounds the moving contact member 41, and is formed at its end nearer the contacts into a series of longitudinal contact fingers 46, biased inwardly by their own resilience and by garter springs 47 to embrace the moving contact member 41.

The stem 44 of the moving contact extends through a bore in a wall of a cylinder 48 formed in the interrupter centre section 16, and carries a piston 49 within the cylinder. The selective admission of compressed air into the cylinder 48 through ports 50 and 51 (Fig. 5), can thus control the movement of the moving contact. Spring biasing is applied to the moving contact through the medium of a torque shaft 52 carrying a lever 53 whose end engages a groove 54 machined in the moving contact stem 44. The torque shaft 52 extends to the outer face of the centre section 16, where it is acted upon by biasing springs.

The compressed air conduit formed by the interrupter support arm 13 divides in the interrupter centre section 16 into divergent inlet passages 60 leading into the annular enclosure 61 surrounding the contacts. Similarly the exhaust passages 62, which are in communication with the interior of the moving contact member 41, converge to form a common exhaust passage leading to the exhaust valve 18. When the interrupter is closed, the engaged surfaces of the contacts form valve surfaces closing the air passage through the interrupter to the exhaust valve; but the contacts are by-passed by one or more bleed apertures, not shown in the drawing, so that the entire interrupter, is in these conditions filled with compressed air.

The exhaust valve 18 comprises a sleeve valve 70 slidable within the valve casing 71 so as to open or close the annular exhaust passage 72 from the interior of the interrupter. A flow deflector 73 forms a guide for the valve. An annular piston 74 is formed around the periphery of the sleeve valve 70 and slides within a cylinder 75 formed within the valve casing. The upper end of this cylinder communicates with the atmosphere through a port 75a, while the lower end communicates through a connection 76 with a control valve for the exhaust valve. Piston by-pass passages 77 are provided to control the movement of the valve. A spring 78 biases the valve to its closed position, in which it engages with an annular seating 79 recessed below the face of the exhaust passage 72; both sides of the piston 74 normally being exposed to atmospheric pressure in the event of spring failure the valve remains biased to its closed position by compressed air supplied through union 76a acting on the differential area of the valve, this differential area resulting from the upper part of the sleeve valve 70 having a slightly greater diameter than the lower part. The valve is substantially balanced in respect of air pressures within the exhaust passage 72, which do not affect its operation.

The immediate control gear for the interrupter assembly is contained within a housing 90 mounted on the side of the interrupter centre section 16. The arrangement is shown in Fig. 4. The torque shafts 52 connected with the moving contacts of the interrupter project into this housing and carry short arms 91. Compression springs 92, each mounted on a rod 92a between a colar 93 pivoted about a fixed point 94 and a further collar 95 connected with one of the arms 91, and free to slide on the rod 92a, constitute the moving-contact biasing springs. Movement of the contact between its closed and open positions is reflected in a rotation of the torque shaft 52 through an angle of about 30 degrees on either side of the line joining the shaft to the spring pivot 94. The toggle formed by the arm 91 and the spring 92 is thus carried over centre with each complete movement of the contact, and the contact is biased by the spring 92 towards its open or its closed state according to its position in its travel.

The rotation of the spring axes about their pivot 94 is also utilised to provide a contact follow-up motion for application to the control gear. Arms 96 carried by the pivoted collars 93 are connected by links 97 to a triangular floating lever 98; the remaining angle of this lever is pivoted on a long pivoted support arm 99 so as to move in a substantially vertical direction, and is also connected by means of a further link 100 to a point on a valve actuating lever 101. This lever is arranged for the actuation of three valves 102, 103, and 104 in the manner to be hereinafter described. It is suspended by a pivoted bell-crank lever 105, the free arm of which is linked to the interrupter control rod 106 (shown broken for clarity). This rod is connected to the main circuit breaker control mechanism and is movable between the positions indicated in the drawing; it is biased towards its upper or "trip" position by a spring 107, so that the rod is normally maintained in tension.

The control linkage just described thus forms a mechanical control scheme for the actuation of the various control valves 102, 103, 104 which exercise the direct control of the interrupters. This arrangement ensures the minimum time delay in the operation of the various parts of the interrupter on the initiation of a circuit breaker operation, and requires only a single control connection between the interrupter pair and the main control cabinet.

The functions of the valves 102, 103, 104 are as follows:

The valve 102 controls the exhaust valve 18, and comprises a balanced sleeve valve 112 mounted on the valve stem 113 and biased by a spring 114 to its closed position. The valve is mounted directly on an inlet flange formed in the interrupter centre section 16 and admitting high pressure air to the annular space surrounding the sleeve valve 112; the valve outlet communicates through the connection 76 with the inlet port of the exhaust valve operating cylinder. The use of a balanced construction for this valve 112 results in an arrangement which, although controlling an air conduit of appreciable cross-section leading to the exhaust valve cylinder 75, with consequent minimum delay in the operation of the exhaust valve, puts a comparatively light load on its actuating mechanism, the employment of a pilot valve for the operation of the control valve 102 being therefore unnecessary.

Valve 103 controls the isolating movement of the arcing contact 29 at the conclusion of an opening operation of the interrupter. In its normal position it admits compressed air through a connection 120 to the interior of the arcing contact cylinder 31, and therefore urges the arcing contact 29 towards its engaged position with the moving contact. When the valve is actuated by depression of its actuating plunger 121, it closes the high-pressure air supply to the cylinder of the arcing contact and exhausts the interior of the cylinder to the atmosphere, permitting the withdrawal of the arcing contact 29 to a retracted position within the main contact 26 to provide an isolating contact gap.

The remaining control valve 104 is a pilot valve for the actuation of a changeover valve 122, for the moving contact operating cylinders, housed within the interrupter centre section, as shown in Fig. 5. This valve comprises a stem extending within a transverse bore in the centre section 16 and provided at one end with a piston 123 sliding within a cylinder 124. A connection 125 connects the cylinder with the control valve 104. Valve members 126 and 127 control the admission of compressed air from an inlet port 128 to the contact actuating cylinders 48 of the pair of interrupters through ports 50 and 51, and also control the exhausting of air within the cylinder to atmosphere through exhaust passages 129 and 130. A spring 131 biases the valve 122 to the position shown in the drawing; operation of the control valve 104 by pressure on its actuating plunger 132 admits compressed air to the inlet 125 of the control cylinder and moves the entire valve 122 to its other extreme position.

The operation of the interrupter assembly through a sequence comprising an opening operation followed by a closing operation will now be described. The sequence commences with the interrupter contacts in their closed positions, as shown in Fig. 2, the various linkages of the control mechanism being in the positions shown in Figs. 4 and 5 and the exhaust valve 18 being closed.

Although in general the sequence of operations will be described with reference to a single interrupter, both interrupters of any given pair will normally operate simultaneously.

With the contacts closed, the resilient contact fingers 27 of each fixed contact engage the outer annular face of the movable throat contact 42, and there is a slight clearance between the contact fingers 27 and the outer face of the arcing contact 29. The main current path through each interrupter thus does not rely on the butt contact between the throat 42 and the arcing contact 29, which are however pressed together by the arcing contact biasing spring 33. The entire interrupter assembly up to the exhaust valve 18 is filled with compressed air. The moving contacts are biased to their closed positions solely by the action of the contact biasing springs 92 acting through their torque shafts 52. There is no pressure difference across the contacts or across their actuating pistons 49, and therefore there is no tendency for the contacts to move.

An opening operation of the interrupter is initiated by moving the control rod 106 upwards from its "close" position to its "trip" position. This action displaces the valve control lever 101 to the left through the medium of the suspending bell-crank 105; the left-hand end of the lever 101 strikes the plunger 113 of the exhaust pilot valve 102 and causes this valve to open. Air under pressure is delivered through connections 76 to the lower face of the exhaust valve control piston 74, overcoming the force of the biasing springs 78 and thus moving the exhaust valve 70 to its open position. The movement of the exhaust valve is buffered towards the end of its stroke by the closure by the piston of the port of the by-pass passage 77.

The exhaust valve 18 now being opened, the passages 62 leading to it from the interior of the moving contacts 41 are exhausted to atmosphere. The bleed passage communicating with the passages from the annular space 61 surrounding the contacts is too small to permit pressure to build up on the outlet side, and the engaged faces of the contacts act as valve surfaces to prevent the flow of air into the hollow moving contact. The effect of the reduction of pressure within the hollow moving contact 41 is thus to produce on that contact an unbalanced force tending to move it away from the fixed contact 24, this movement being assisted in its initial stage by the biasing spring 33 of the arcing contact 29. The initial movement of the moving contact 41 moves the annular outer contact face of the throat contact 42 out of engagement with the resilient fixed contact fingers 27, which move inwardly to engage the outer surface of the arcing contact 29. Movement of the arcing contact 29 and the throat contact 42 continues with the contacts in engagement until the arcing contact 29 reaches the end of its travel.

The initial movement of the moving contact, which is effected against the action of its biasing spring 92, moves the contact actuating piston 49 sufficiently to uncover the inlet port 50 of its cylinder, permitting the flow of high-pressure air into the cylinder through this port. Since the other side of the piston 49 is exhausted to the atmosphere through the port 51, the valve 127 and the exhaust passage 129, the pressure difference across the piston assists in accelerating the moving contact against the diminishing resistance offered by its biasing spring 92. The initial phase of the opening operation ends with the separation of the engaged faces of the arcing contact 29 and the throat contact 42. This permits the initiation of a blast of air through the interior of the hollow moving contact 41 and the exhaust valve 18 to the atmosphere and also, if the interrupter is opening in live circuit conditions, draws an arc between the arcing ring 140 of the throat contact and the annular arcing insert 141 of the arcing contact. The air blast flowing into the throat contact immediately transfer this arc to the central arcing area 142 of the arcing contact and to the arcing probe 44a of the moving contact assembly, so that only the initial flash is carried by the two arcing rings 140, 141. It will be observed that the main current-carrying contact surfaces do not have to perform any arcing duty.

The movement of the interrupter moving contacts towards their open circuit positions is reflected in the movement of the links 91 forming part of the biasing toggle arrangement, this movement carrying the toggle over centre at about the instant of contact separation so that the springs now tend to assist the piston 49 in driving the contact rapidly to its fully open position. The contact movement buffered towards the end of the stroke by means of a protuberant boss 143 formed in the face of the contact piston 49, which enters the cylinder exhaust port 51 and restricts the flow of air through it.

Fig. 3 of the drawings shows the position of the contacts 24, 40 and the exhaust valve 18 as the moving contact assembly approaches the end of its opening travel.

Thus an opening operation of the interrupters is initiated solely by causing the exhaust valve 18 to open. The movement of the contacts during the operation is reflected in the rotation of the links 96 secured to the pivoted spring collars 93, tending to draw downwards each of the links 97 secured to them. The resultant downward movement of the floating lever 98 is therefore dependent on the total contact movement of the two interrupters; after a displacement indicating that both the interrupter contacts have almost reached their fully open positions, the left-hand end of the control lever 101 clears the plunger 113 of the valve 102 and allows this valve to reset. The compressed air acting on the lower face of the exhaust valve control piston 74 is allowed to escape through a bleed aperture, and the exhaust valve resets to its closed position under the action of its biasing springs 78 and of the air pressure on the differential area of the valve. The blast of air through the interrupters ceases, and both interrupters remain fully charged with compressed air. The final movement of the valve control lever 101 depresses the actuating plunger 121 of the isolating contact control valve 103, exhausting the interior of the arcing contact cylinder 31 to the atmosphere and allowing the arcing contact 29 to withdraw within the contact fingers 27, under the action of the air pressure

within the interrupter, to provide a contact gap adequate for circuit isolation at atmospheric pressure. The opening operation is now completed.

Since the downward displacement of the floating lever 98, and hence that of the left-hand end of the valve control lever 101, is dependent on the total contact movement of the two interrupters, failure of one interrupter to operate simultaneously with the other will result in the exhaust valve remaining open, and in the maintenance of the air blast through both interrupters, until both interupters have finished their opening operations.

At the completion of an opening operation, the interrupter contacts are held in their open positions by the action of the biasing springs 92.

To initiate a closing operation of the interrupters the control rod 106 is moved downwardly to return it to its "close" position. The first result of this is that the valve control lever 101 is moved bodily to the right by the rotation of bell-crank lever 105; the left-hand end of the lever 101 clears the striker 121 of the isolating control valve 103, allowing this valve to reset and allowing arcing contact 29 to move out beyond the ends of the fixed contact fingers 27 under the action of its biasing spring 33 and the air pressure in the cylinder 31.

The right-hand of the valve control lever 101 actuates the striker 132 of the pilot valve 104, which operates to admit air under pressure to the actuating cylinder 124 of the changeover valve 122. By this movement port 50 of the contact actuating cylinder 48 is exhausted to the atmosphere through the exhaust passage 130, and the outer port 51 of the cylinder is supplied with high-pressure air through the port 128. The pressure unbalance across the piston 49 overcomes the action of the biasing spring 92 and drives the moving contact towards its closed position. The toggle levers 91 pass over-centre in the reverse direction and the springs 92 then bias the contacts towards their closed positions; the movement of the contacts is reflected in the upward movement of the floating lever 98, in correspondence with the pivotal movement of the springs, and consequently the valve control lever 101 pivots in a clockwise sense about its point of attachment to the bell-crank lever 105.

The throat contact 42 engages the arcing contact 29 and carries the latter with it as it continues its movement. As the contacts approach the end of their travel, the throat contact 42 engages the contact fingers 27 with its outer annular face, lifting the contact fingers clear of the arcing contact 29 and providing the main current connection through the interrupter. When the contact movement is almost completed, the right-hand end of the valve control lever 101 clears the striker of pilot valve 104; the latter resets and cuts off the compressed air supply to the actuating cylinder of the changeover valve 122, which also resets.

The complete interrupter and associated mechanism is now reset in readiness for a further trip operation.

At any stage during the closing operation, the operation may be reversed and the interrupters returned to their open state simply by moving the control rod 106 to its "trip" position; this action reverses the setting of the pilot valve 104, and hence that of the changeover valve 122, reversing the motion of the contacts, and except in the extreme initial stages of the closing operation actuates the pilot valve 102 to open the exhaust valve. The remainder of a normal tripping operation follows. The mechanism is thus effectively "trip-free".

Figs 6 and 7 of the drawings show how the control rods 106 of the two interrupter pairs 14 mounted on an insulator 11 pass down the support arms 13 and in the insulator top cap 12 are connected through a bell-crank lever 150 with a single control rod 151 passing down the support insulator. This single rod is maintained in tension by a spring 152 at its upper end. At the lower end of the insulator, a further control rod 153 connects the linkage with a common operating rod 154 connected with the operating mechanism housed in the control cabinet 19. All the control rods are thus maintained in tension by their loading springs, which also serves to accelerate the rods from their "close" position to their "trip" position on the initiation of a tripping operation; (alternatively only the actual interrupter control rods 106 may be tensioned, being connected with the control mechanism by a rotary or other positively-acting linkage). The mechanism in cabinet 19, which is of the "trip-free" type, includes a latch by which the operating rods are maintained in the "close" position against the action of the loading springs; a tripping operation is initiated by releasing this latch and allowing the loading springs to move the rods to the trip positions. The control rods are restored to their "close" position and a closing operation initiated by a suitable motor, either pneumatically, hydraulically, or electrically operated, which latches the rods in the "close" position against the action of the springs. The common operating rod 154, which is also tensioned by a loading spring 155, may pass from the mechanism cabinet 19 to other circuit breakers associated with that shown in the drawing; thus the units of a three-phase circuit breaker may be operated simultaneously by a common control mechanism.

We claim :

1. A gas blast electric circuit breaker including two gas blast circuit interrupters arranged for simultaneous operation and having separate contact enclosures which are arranged for permanent communication with a common source of compressed gas and which communicate with the atmosphere through a common exhaust valve, the opening of said exhaust valve causing a blast of gas to flow through the two contact enclosures during opening operation of the circuit breaker.

2. A gas blast electric circuit breaker as claimed in Claim 1 in which the separating movement of the contacts of the two circuit interrupters at the beginning of an opening operation of the circuit breaker is dependent upon or made in correspondence with the opening of the exhaust valve.

3. A gas blast electric circuit breaker as claimed in Claim 1 or Claim 2 in which the enclosures are formed by tubular insulators projecting one from each side of a common centre section, which supports the exhaust valve and also forms the connections to the common source of compressed gas, the gas blast produced during operation of the circuit breaker thus passing outwardly from the centre section to the interrupters and returning inwardly to be exhausted through the exhaust valve.

4. A gas blast electric circuit breaker as claimed in any of Claims 1 to 3 in which the two interrupters are electrically connected in series.

5. A gas blast electric circuit breaker as claimed in Claim 3 in which the two interrupters are electrically connected in series by the common centre section.

6. A gas blast electric circuit breaker as claimed in Claim 1, wherein a movable valve member of the exhaust valve is arranged for permanent biasing towards its closed position by compressed gas acting on a differential area of the valve member.

7. A gas blast electric circuit breaker as claimed in Claim 6, wherein the valve member is in addition biased towards its closed position by a spring.

8. A gas blast electric circuit breaker including two or more pairs of interrupting contacts, the movable contacts of the pairs being arranged for simultaneous actuation but having no positive mechanical connection between them, a common valve for controlling a blast of gas through separate contact enclosures for the pairs of contacts and arranged to open at the beginning of an opening operation of the circuit breaker, and means for allowing the said valve to close only after a predetermined total movement of all the movable contacts of said pairs of contacts towards their open positions.

9. A gas blast electric circuit breaker as claimed in Claim 8 having two pairs of associated interrupting contacts, wherein said means includes a lever having two points in its length connected so as to move in correspondence with the respective movement of the movable contacts, and having a third intermediate point connected with closing means for said valve so

as to allow the valve to close after a predetermined movement of said third point.

10. An electric circuit breaker including a power driven contact actuating mechanism and a control member linking the contact actuating mechanism with a remotely situated primary actuating mechanism, the control member being movable between "close" and "trip" positions to initiate corresponding operations of the circuit breaker, and being spring biased to its "trip" position.

11. An electric circuit breaker as claimed in Claim 10, wherein the biasing spring acts on the end of the control member nearer the contact actuating mechanism to place the control member under tension, at least when in its "close" position, in which it is held by a releasable latch in the primary actuating mechanism, said latch constituting the circuit breaker tripping control.

12. An electric circuit breaker substantially as herein described with reference to and as illustrated in the accompanying drawings.

R. HALL

OF REMFRY & SON,

Agent for the Applicants.

Dated this 27th day of December 1960.

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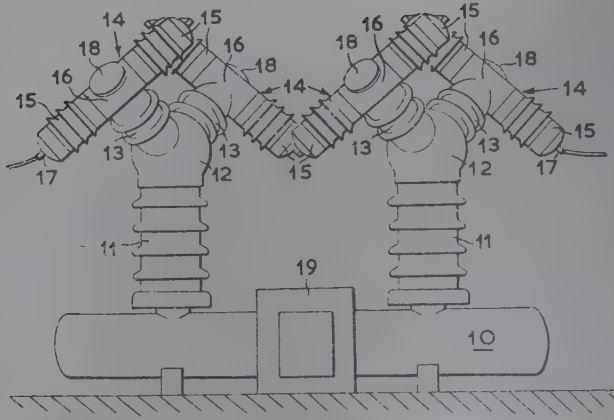

FIG. 1

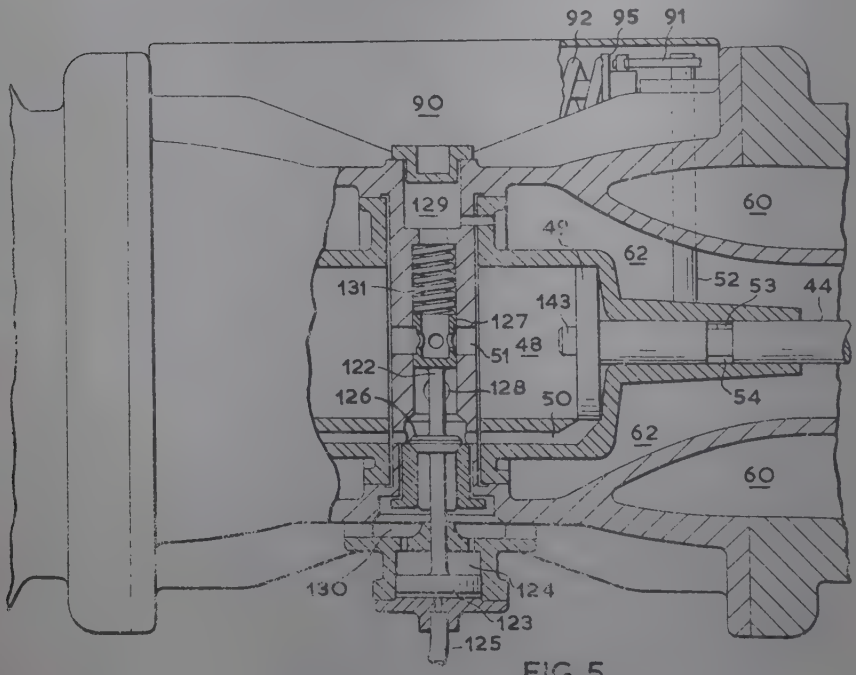

FIG. 5

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FIG. 2

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FIG. 3

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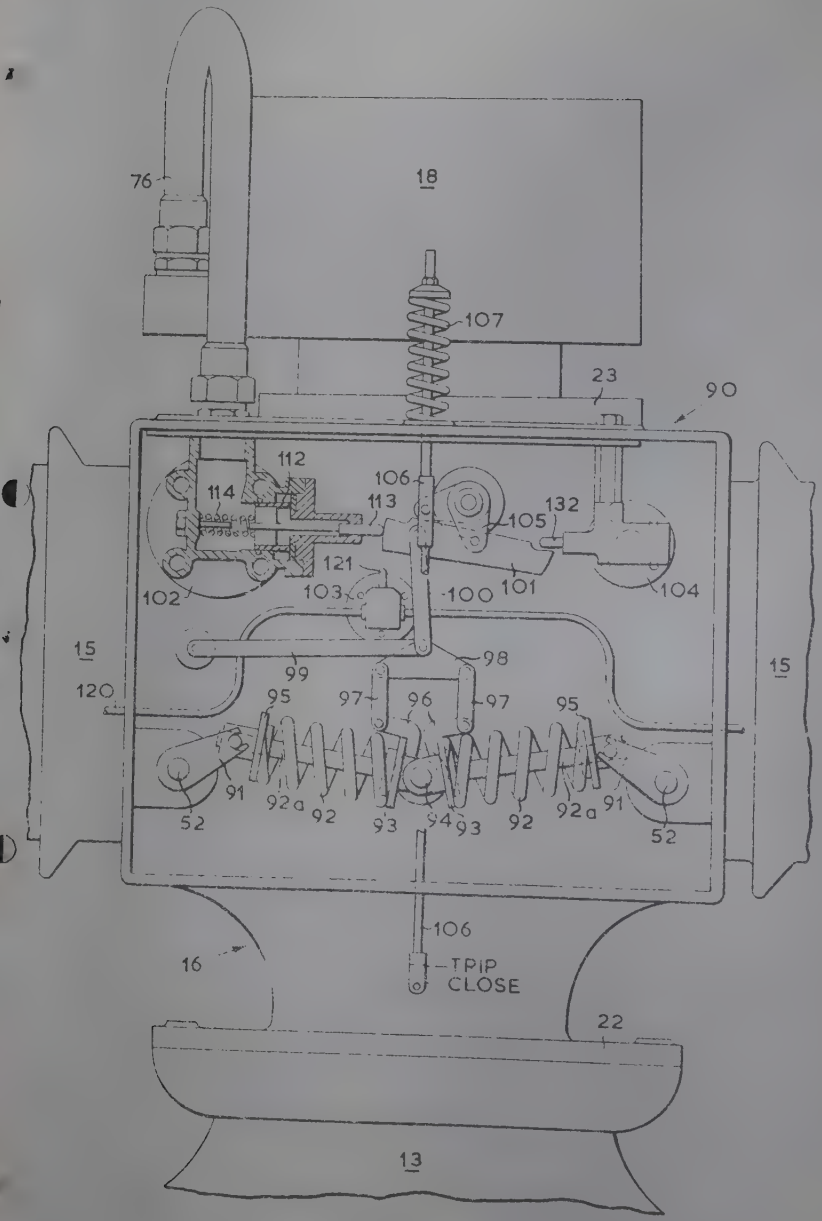

FIG. 4

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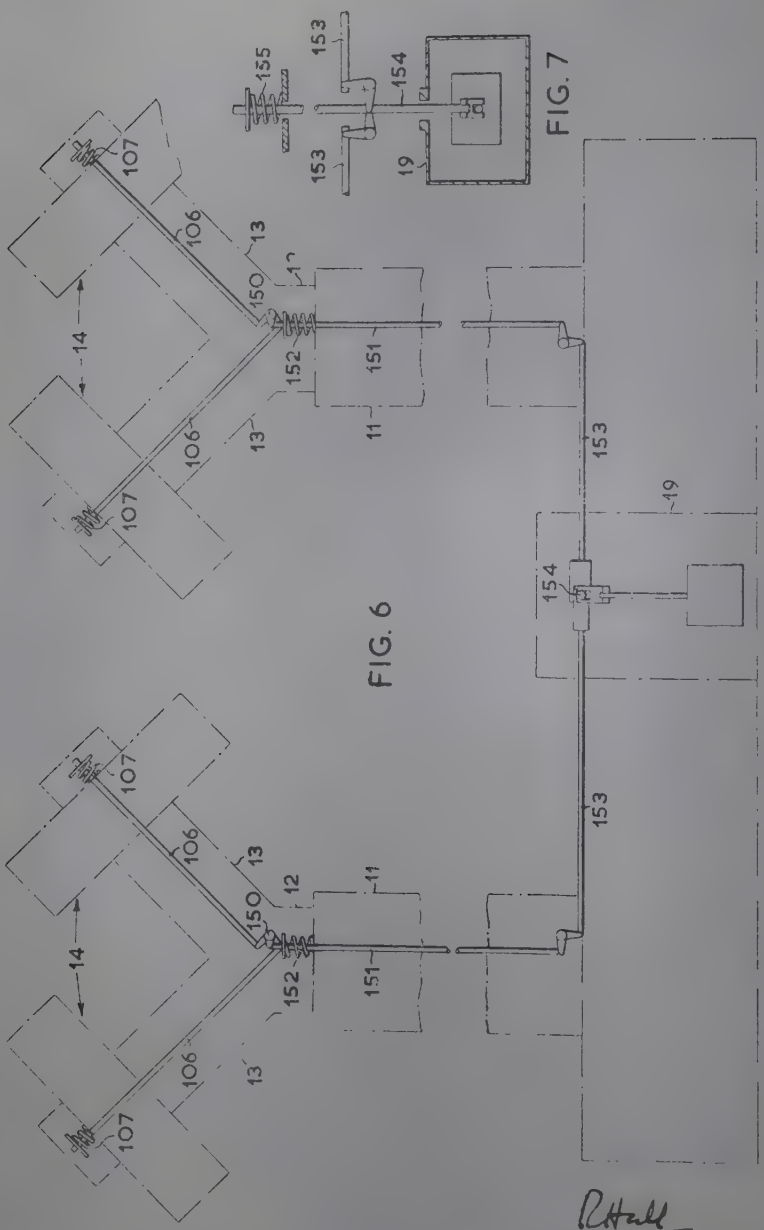

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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.
Specification No. 74693, filed 27th December 1960./6 Paus 1882 (Saka). Reciprocity date (United Kingdom) 14th January, 1960. (Accepted 7th February 1962).

"IMPROVEMENTS IN HORIZONTAL BORING AND LIKE MACHINE TOOLS."

H. W. KEARNS & CO. LIMITED, A British Company, of Atlantic Street, Broadheath, near Manchester, England, Engineers.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This invention relates to horizontal boring and like machine tools, including such machines designed to carry out also such operations as drilling, tapping, turning, facing and milling, and its object is to provide means for quickly and accurately securing a tool mandrel in the forward end or nose of the spindle of such a machine.

The tool mandrel usually has a conical spigot to seat in a conical socket in the spindle nose and for accurate work it is essential that the mandrel, on which the tool is previously accurately mounted, should be held truly axially in the spindle and firmly secured. The securing means should be capable of quick engagement and release, to avoid waste of time in tool changing, and should also not be liable, through over-tightening for example, to cause distortion of the mandrel and spindle seating.

According to the invention there is provided a horizontal boring or like machine tool spindle within which a coaxial axially movable draw bar is provided with means at its outer end for releasably engaging a tool mandrel to be held in the spindle, the draw bar is axiallys pring-loaded to draw a tool mandrel on the draw bar into position in the spindle and means are provided for moving the draw bar axially against its spring-loading to project from the spindle a tool mandrel on the draw bar for removal therefrom.

The above arrangement enables a tool mandrel to be drawn into place and held in the spindle by a spring load designed to be sufficient to ensure repeatedly accurate seating of the mandrel in the spindle but limited so that an excess load, greater than the parts can withstand without distortion, cannot be applied.

If a preferred construction, the spring-loading is provided by a helical compression spring coaxially surrounding the draw bar in the spindle, the outer end of the draw bar is provided with one member of a bayonet-type joint, for engagement by the tool mandrel as the other member, and the means for moving the draw bar axially against its spring-loading, for removal of the tool mandrel, comprises a pressure-fluid operated ram, conveniently provided by a piston on the draw bar working in the spindle as a cylinder.

One embodiment of a preferred construction of the invention is shown on the accompanying drawing which is an axial section through the tool spindle of a horizontal boring machine tool.

The spindle 1, which has lower and upper key-ways 2, is rotatable mounted by a bearing 3 in the headstock or spindle slide of the machine in the usual manner.

A liner 4 in the spindle is formed at the forward end or nose as a conical socket 5 for the correspondingly conical spigot 6 of a tool mandrel 7, in which a tool is mounted by its shank 8, and drive keys 9 are provided as usual between the mandrel and the end of the spindle.

Screwed axially into the inner end of the mandrel spigot 6 is an adaptor 10 the inner end of which is formed as a bayonet socket the throat of which has four internal segmental lobes 11 for axial and rotary engagement with the correspondingly lobed cruciform head 12 of a bayonet spigot 13 screwed axially into the outer end of a draw bar 14 which is mounted to slide coaxially in the spindle liner 4.

Near its inner end, the draw bar 14 is necked and embraced by a collar 15, diametrally split and secured by chord screws in holes 16, and this collar 15 retains a helical compression spring 17 surrounding the draw bar 14 in an enlargement of the bore of the liner 4.

The spring 17 thrusting against the collar 15 tends constantly to draw bar 14 axially into the spindle to seat the tool mandrel spigot 6 in the socket 5. The spring 17 is disigned so that its thrust cannot cause any distortion at the mandrel seating whilst being sufficient to ensure full abutment of the conical seating surfaces.

Beyond the collar 15, the draw bar 14 is splined to slide in a bearing sleeve 18, preferably of phosphor-bronze to avoid stiction, and the inner end of the draw bar carries fast a piston 19 which operates as a hydraulic or pneumatic ram in a cylinder-end 20 of the spindle.

The outer end of the cylinder 20 is closed by a cover 21 to which is connected by a swivel coupling 22 a pipe 23 for supply of fluid under pressure to the cylinder 20.

When the cylinder 20 is placed under pressure, the piston 19 is displaced, to the right as seen in the drawing, and overcoming the thrust of the spring 17, moves the draw bar axially far enough for the mandrel 7 to be removed, after release of the keys, by turning and withdrawal from its bayonet joint.

The draw bar 14 is held against turning, by the splined bearing sleeve 18, and the cruciform head 12 of the bayonet spigot 13, screwed home tight, has a constant angular position which ensures that, when engaged by the adaptor 10, the tool mandrel 7 is correctly angularly positioned for engagement of the keys 9.

When the tool mandrel has been engaged with the draw bar, release of the fluid pressure supplied to the cylinder 20 permits the spring 17 to recover and draw the tool mandrel spigot 6 firmly into accurate, truly axial, seating in the spindle nose socket 5.

It will be seen that all the internal components of the spindle are symmetrically disposed about the axis of the spindle which thus enables a high degree of balance to be maintained during running.

It will also be noted that the fluid pressure is applied only for tool removal so that, should there be a failure in fluid supply, the mechanism will "fail safe", the spring maintaining the draw bar retracted and the tool mandrel held.

WE CLAIM :—

1. A horizontal boring or like machine tool spindle within which a coaxial axially movable draw bar is provided with means at its outer end for releasably engaging a tool mandrel to be held in the spindle, the draw bar is axially spring-loaded to draw a tool mandrel on the draw bar into position in the spindle and means are provided for moving the draw bar axially

against its spring-loading to project from the spindle a tool mandrel on the draw bar for removal therefrom.

2. A spindle according to claim 1, in which the spring-loading is provided by a helical compression spring coaxially surrounding the draw bar in the spindle.

3. A spindle according to claim 1 or 2, in which the outer end of the draw bar is provided with one member of a bayonet-type joint for releasable engagement with a tool mandrel provided with the other member of the joint.

4. A spindle according to claim 3, in which the bayonet joint member on the draw bar is an axial spigot in screw-thr-aded engagement with the draw bar and having a cruciform or like lobed head for axial and rotary engagement by a correspondingly internally lobed socket member on a tool mandrel.

5. A spindle according to any of the foregoing claims, in which the means for moving the draw bar axially against its spring-loading comprises a pressure-fluid operated ram in the spindle.

6. A spindle according to claim 5, in which the ram comprises a piston mounted on the draw bar and the spindle provides a cylinder therefor.

7. A horizontal boring machine tool spindle provided with a spring-loaded draw bar for a tool mandrel and a fluid-pressure operated ram therefor substantially as described with reference to the accompanying drawing.

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Agent for the Applicants.

Dated this 27th day of December 1960.

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H. W. KEARNS & CO. LTD.
No. 74693 of 1960.

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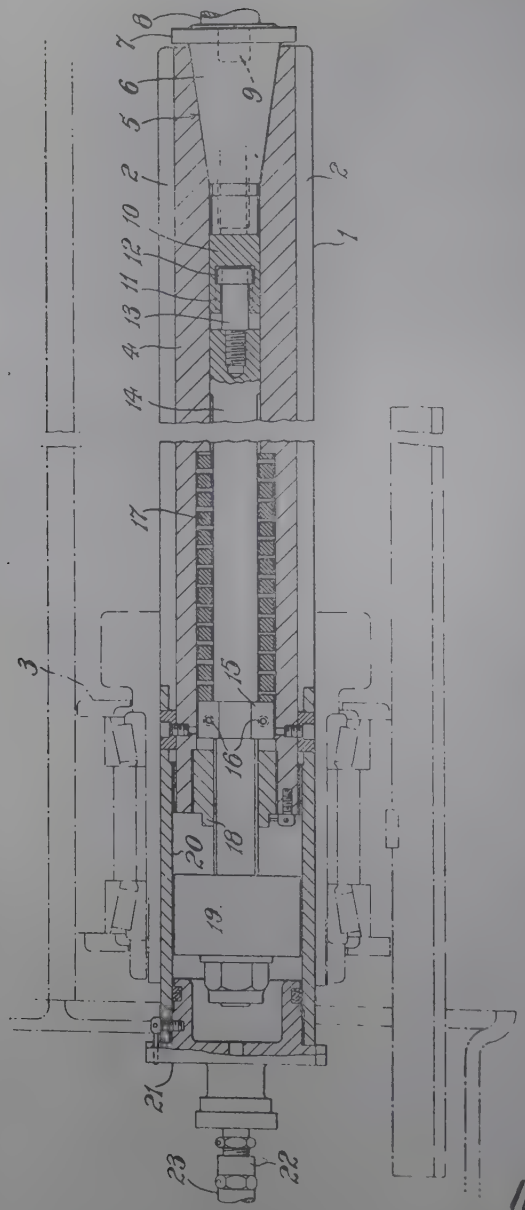

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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74697, 27th December 1960. 6 Paus 1882 (Saka) (Accepted 4th May 1962.)

PROCESS FOR THE MANUFACTURE OF LINEAR QUINACRIDONES.

CIBA LIMITED, Chemical Manufacturers, a Swiss Corporation, of Klybeckstrasse 141, Basle, Switzerland.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention provides a process for the manufacture of quinacridones or dihydroquinacridones by the ring closure on both sides of 2 : 5-diarylamino-terephthalic acids or 2 : 5-diarylamino-3 : 6 dihydro-terephthalic acid esters, in the presence of aluminum chloride.

As starting materials there are used more especially 2 : 5-diphenylamino-terephthalic acid or 2 :5-diphenyl-amino-3 : 6-dihydro-terephthalic acid diethyl or dimethyl ester or substitution products thereof substituted in the phenyl radicals, for example.

2 : 5-Di(methylphenylamino)-terephthalic acids,
2 : 5-Di-(methoxyphenylamino)-terephthalic acids,
2 : 5-Di-(halogen-phenylamino)-terephthalic acids,
2 : 5-Di(nitrophenylamino)-terephthalic acids,
2 :5-Di- (2′ :4′- dimethyl-phenylamino) -terephthalic acid,
2 : 5-Bis-(4′-diphenylamino)-terephthalic acid and
2 : 5-Dianilido-2′ : 4′ : 2″ : 4″- tetrachloroterephthalic acid.

There may also be used 2 :5-diarylamino-terephthalic acids, which contain as the aryl radical a polycyclic radical, for example, a naphthalene, phenanthrene or pyrene radical.

The aforesaid 2 :5-diarylamino-dihydro-terephthalic acid esters can be obtained by known methods, for example, by condensing a succinylo-succinic acid ester with aniline or a derivative of aniline, and the aforesaid 2 : 5-diarylamino-terephthalic acids can be obtained by oxidizing a corresponding dihydro-ester and hydrolysing the resulting 2 : 5-diarylamino-terephthalic acid ester.

The starting materials are advantageously introduced into an aluminium chloride melt. As pure aluminum chloride has a relatively high melting point it is of advantage to add an agent that lowers the melting point. As such agents there may be mentioned, for example, sodium chloride, sodium fluoride, calcium chloride, potassium chloride, magnesium sulfate, sodium sulfite and sulfur dioxide. The yield and purity of the final product can be very favourably influenced by the addition, of an agent capable of splitting-off water, for example, phosphorus pentoxide. There is advantageously used at least 0.5 part, and advantageously at least one part, of phosphorus pentoxide for each part of 2 : 5-diarylamino-terephthalic acid or of the corresponding dihydro-ester.

As agents for lowering the melting point there may also be used high boiling inert organic solvents, especially ortho-dichlorobenzene, or the reaction may be carried out in a suspension of aluminum chloride in such a solvent.

There are advantageously used at least two parts of aluminum chloride for each part of the 2 :5-diarylamino-terephthalic acid or the corresponding dihydro ester.

The temperature is generally so chosen that the reaction mixture can be stirred. There are advantageously used temperatures above 100°C, for example, within the range of about 120°C to 200°C or, in certain cases, above 200°C.

After the reaction the reaction mixture is advantageously introduced into ice or water, whereupon the quinacridone or dihydroquinacridone precipitates out, and it is then filtered off. The quinacridones so obtained can be purified in the usual manner, for example, by dissolution in concentrated sulfuric acid followed by dilution with water, advantageously to sulfuric acid of about 80% strength, whereupon the quinacridone precipitates in a crystalline form. The products so obtained, can be converted by one of the usual grinding methods into a form suitable for use as pigments.

The dihydroquinacridones obtained by the process can be converted into the corresponding quinacridones by treatment with an oxidizing agent, for example, a nitrobenzene sulfonate.

Numerous processes for converting 2 :5-diarylamino-terephthalic acids by ring closure into the linear quinacridones are known, such as heating the starting material in the presence of zinc oxide, phosphorus pentachloride, phosphorus pentoxide or the like. All these processes give poor yields, and can generally only be used in special cases. The best method known hitherto is to heat the 2 :5-diarylamino-terephthalic acid in molten boric acid at a temperature above 300°C (Annalen vol 518, page 245) However, this method is extremely difficult to carry out industrially, on the one hand, owing to the high temperature used, and, on the other, owing to the frothing property of the boric acid melt and the fact that it finally solidifies to a non-stirrable mass.

Journal für prakt. Chemie, volume 102, page 355 (1921) describes the cyclization of 4,6-diphenylamino-isophthalic acid dichloride with aluminum chloride to form the angular quinacridone. In the case of 2,5-diphenyl-amino-terephthalic acid dichloride, however, this process fails completely. It is therefore surprising that 2,5-diaryl-amino-terephthalic acids can be cyclicized with aluminum chloride to give a good yield of linear quinacridone.

The following Examples illustrate the invention, the parts and percentages being by weight :—

Example 1.

A mixture of 80 parts of aluminum chloride and 20 parts of sodium chloride is heated at 120°C until a clear melt is obtained. 10 parts of 2 : 5-diphenylamino-terephthalic acid are introduced and the mixture is heated in the course of one hour to 180°C. That temperature is maintained for three hours and then the melt is poured on to 400 parts of ice, acidified with hydrochloric acid, boiled for a short time, and the precipitated product is filtered off and extracted at the boil for one hour with 1000 parts of caustic soda solution of 5% strength.

There are obtained 8.8 parts of a crude linear quinacridone which can be purified, for example, by dissolution in sulfuric acid followed by dilution to a concentration of 80%.

Example 2.

By introducing 11.1 parts of para-ditoluidino-terephthalic acid into a melt of 80 parts of aluminum chloride and 20 parts of sodium chloride, and working up as described in example 1, there are obtained 10 parts of the corresponding dimethyl-quinacridone.

Example 3.

10 parts of dianilido-terephthalic acid are introduced into a melt of 88 parts of aluminum chloride, 20 parts of sodium chloride and 15 parts of phosphorus pentoxide at 120°C. The reaction mixture is cautiously heated to 180°C and maintained at that temperature for two hours. By working up in the usual manner there are obtained 8.7 parts of quinacridone of high purity.

Example 4.

50 Parts of aluminum chloride and 10 parts of sodium chloride are melted at 140°C. 10 Parts of dianilido-terephthalic acid are slowly introduced into the melt. Then 30 parts of urea are rapidly added, whereupon the temperature rises spontaneously to 160°C. The whole is further heated and stirred for two hours at 180°C. The melt is introduced as hot as possible into ice-water. The further working up is the same as described in Example 1. and there is obtained a quinacridone having similar qualities.

Example 5.

18 Parts of aluminum chloride are introduced at room temperature into 100 parts of ortho-dichlorobenzene, and the whole is cautiously heated to 100°C. At that temperature 10 parts of dianilido-terephthalic acid are introduced. The whole is then heated to 190°C, and the reaction is carried on for two hours. The whole is then cooled to 120°C, poured into water, and the mixture is acidified with hydrochloric acid and filtered with suction. The press cake is first freed from ortho-di-chlorobenzene by means of hot

Price : TWO RUPEES.

alcohol, and is then washed with water until free from acid. After purification with alkali, there are obtained 8.9 parts of quinacridone.

Example 6.

50 Parts of aluminum chloride are introduced at room temperature into 80 parts of ortho-dichlorobenzene, and the whole is then heated to 100°C. 10 Parts of dianilido-terephthalic acid are added to the melt, and the whole is heated for three hours at 180°C. By working up as described in Example 5 there are obtained 8.1 parts of quinacridone.

Example 7.

12.9 Parts of 3 : 6-dihydro-2 : 5-dianilido-terephthalic acid diethyl ester are introduced into a melt of 88 parts of aluminum chloride and 20 parts of sodium chloride at 130°C. The whole is then reacted for 3 hours at 180°C, and the reaction mixture is poured into water, acidified with hydrochloric acid and filtered with suction.

The dihydroquinacridone so obtained can be oxidized by known methods, for example, by heating it with sodium nitrobenzene-meta-sulfonate in an organic solvent in the presence of an alkali to form quinacridone.

We claim :

1. A process for the manufacture of quinacridones or dihydroquinacridones by the ring closure on both sides of 2 :5-diarylamino-terephthalic acids or 2 :5-diarylamino-3 :6-dihydro-terephthalic acid esters, wherein the reaction is carried out in the presence of aluminum chloride.

2. A process as claimed in Claim 1, wherein the reaction is carried out in an aluminum chloride melt.

3. A process as claimed in Claim 2, wherein phosphorus pentoxide is present in the melt.

4. A process as claimed in Claim 2 or 3, wherein the melt contains a substance that lowers its melting point.

5. A process as claimed in Claim 1, wherein the reaction is carried out in a high boiling inert organic solvent.

6. A process as claimed in Claim 5, wherein ortho-dichlorobenzene is used as the organic solvent.

7. A process as claimed in any one of Claims 1 to 6, wherein at least two parts of aluminum chloride are used for each part of the 2 :5-diarylamino-terephthalic acid or dihydro ester derivative thereof.

8. A process as claimed in any one of Claims 1 to 7, wherein the reaction is carried out at a temperature within the range of 120 to 200°C.

9. A process for the manufacture of a quinacridone or a dihydroquinacridone conducted substantially as described in any one of the Examples herein.

10. Quinacridones or dihydroquinacridones whenever made by the process claimed in any one of Claims 1 to 9.

B. DrPENNING

or DrPENNING & DrPENNING,

Agent for the Applicants.

Dated this 27th day of December 1960.

MGIP Santh.—SL—38 Patent/62—22-2-63—100.

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74698, filed 27th December 1960. (Divided out of No. 67413.) [Ante-dated to 20th April 1959 under Section 5 of the I. P. & D. Act 1911.] (Accepted 11th January 1961.)

AN ELECTROLYTE FOR TREATING METALS.

KAISER ALUMINUM & CHEMICAL CORPORATION, a Corporation organized under the laws of the State of Delaware, of 1924 Broadway, Oakland, California, United States of America.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to oxide coatings on aluminium metal, and the provision of an electrolyte therefor.

For many purposes aluminium surfaces are protected by an oxide coating produced on the surface by exposure as an anode in an acid electrolyte capable of yielding oxygen on electrolysis, such as an aqueous solution of sulfuric acid. The operation of forming such coatings is commonly termed "anodizing" and the aluminium surface thus protected is commonly termed "anodized". Electrolysis in solutions of sulfuric acid with direct or alternating current generally provide colorless to grayish layers of oxide coating on aluminium. The abrasion resistance of these layers is in general not very great which can be demonstrated by the fact that the oxide layer can generally be scraped off with a knife. It has long been desired to produce abrasion resistant oxide layers and to produce colored oxide coated aluminium surfaces. In the past, however, abrasion resistant oxide layers were produced only by anodizing at low temperatures, *i.e.* from about 0° to 30°F. Such process possesses certain inherent disadvantages particularly with regard to the necessity for expensive refrigeration equipment to maintain the coating bath at temperatures below 30°F.

With regard to producing colors on oxide coated aluminium surfaces, in the past it has been necessary to first anodize the aluminium metal base and thereafter dye the anodic coating with organic dye. Another prior art process for producing colored aluminium surfaces is the ferric oxalate hydrolysis process which deposits ferric oxide or hydrate in the pores of the anodic coating. This process requires first anodizing the aluminium metal base followed by immersion of the anodized aluminium in a solution of ferric ammonium oxalate at controlled concentration, temperature and pH. A third means for producing colored aluminium surfaces involves the double precipitation of an insoluble colored inorganic compound. Such processes possess certain inherent disadvantages particularly with regard to the number of processing steps required to produce a colored surface. For example such prior art processes require the anodized metal to be subjected to at least one additional processing step in order to color the anodic coating. In addition where the color is produced by impregnating the anodic coating with a dye, the colors tend to fade rapidly when exposed to ultraviolet light.

According to the present invention an electrolyte for the anodic oxidation of aluminium metal consists essentially of an aqueous solution of sulfosalicylic acid and at least one substance selected from the group consisting of metal sulfates and sulfuric acid. The aluminium metal may comprise a single layer or multiple layers of the same or differing aluminium metals bonded together.

In general the electrolytes of this invention consist essentially of an aqueous solution of from about 5 to 50% by weight of sulfosalicylic acid and at least one substance selected from the group consisting of metal sulfates and sulfuric acid in an amount equivalent to not more than 15% by weight sulfuric acid. Even a small amount of metal sulfate or sulfuric acid is beneficial to the electrolyte embodying the principles of this invention, *e.g.* an amount of metal sulfate or sulfuric acid equivalent to 0.1% by weight of sulfuric acid is beneficial. The preferred ranges are from about 7 to 15% by weight sulfosalicylic acid and an amount of metal sulfate or sulfuric acid equivalent to from about 0.3 to 4% by weight sulfuric acid. It has been found that anodic coatings on samples of various aluminium alloys anodized in electrolytes having compositions within the broad ranges recited above, had superior abrasion resistance as demonstrated by the fact that the coatings could not be easily scraped off with a knife.

For the anodic treatment of the aluminium metal in the electrolyte according to the present invention, there can be provided either alternating or direct current or if desired, combinations of both.

The following Table lists typical aluminium alloys 1100, 5052, 6061-T6 and 7075-T6 which were anodized for 60 minutes in electrolytes embodying the principles of this invention and in a sulfuric acid electrolyte of the prior art.

The electrolytes indicated in the following Table are designated according to the percentage of sulfosalicylic acid and sulfuric acid or ferric sulfate contained therein, the balance of each electrolyte being water. All percentages are by weight of the total electrolyte.

All the samples referred to in the Table were anodized with direct current at 72°F. The current densities employed were 27 a.s.f. for samples anodized in the electrolytes of this invention and 12 a.s.f. for the samples anodized in the sulfuric acid electrolyte. Current densities appreciably higher than 12 a.s.f. generally cannot be employed commercially for anodizing in straight sulfuric acid electrolytes since the resulting coatings are unsatisfactory. In general the voltages necessary to maintain a given current density vary with the cell and the anodizing conditions and the required voltage varies as the anodizing progresses. In anodizing the samples of the said Table the voltages required to maintain a constant current density of 27 a.s.f. ranged from about 25 to 60 volts while the voltages required to maintain a constant current density of 12 a.s.f. ranged from about 12 to 16 volts.

The samples anodized in the sulfosalicylic acid-sulfuric acid anodizing baths were tested for abrasion resistance with an abrasive jet apparatus of the type recommended by the ASTM for testing abrasion resistance. This is described by Roberts A.G., Crouse W. A. and Pizer R. S. "Abrasive Jet Method for Measuring Abrasion Resistance of Organic Coatings," ASTM Bulletin No. 208, September 1955. With this apparatus abrasion resistance is measured by the time required to penetrate the coating and the results are given in the said Table. In general for purposes of comparative data, several spots on each surface to be tested are abraded with the apparatus, the same number of spots being abraded on each sample. The comparative abrasion resistance is then measured by the total time required to penetrate all the spots of the sample. In the Table below, hardness is measured in terms of the total number of seconds required to penetrate ten spots on the sample.

TABLE.

TYPICAL ALUMINIUM ALLOYS ANODIZED IN ELECTROLYTES OF THIS INVENTION AND IN PRIOR ART SULFURIC ACID ELECTROLYTE

	10% Sulfosalicylic Acid, 1% Sulfuric Acid Electrolyte.	10% Sulfosalicylic Acid, 2% Sulfuric Acid Electrolyte.	15% Sulfosalicylic Acid, 3% Ferric Sulfate Electrolyte	15% Sulfuric Acid Electrolyte.
Alloy	Abrasion Resistance	Abrasion Resistance	Abrasion Resistance	Abrasion Resistance
1100	33.0	19.0	27.9	11.5
5052	22.5	22.5	30.3	12.0
6061—T6	25.0	19.5	31.6	11.5
7075—T6	31.0	21.5	—	7.0

It is readily seen from the results indicated above that the anodic oxide coatings produced on the aluminium base metal employing the electrolytes of this invention are superior in abrasion resistance to the oxide coatings produced with

conventional sulfuric acid electrolytes. The above samples were characterized by attractive, light stable colors. However, for optimum results with regard to the production of colored surfaces on the aluminium alloys it is preferred to use an electrolyte with a sulfuric acid content of less than about 1%, *e.g.* 1 to 1%.

As used herein, the term "aluminium" is meant to cover high purity aluminium, commercial purity aluminium and aluminium alloys.

It will be understood that various changes, omissions and additions may be made to this invention without departing from the spirit and scope thereof as set forth in the appended claims.

All percentages in the claims are by weight of the total electrolyte.

This application has been divided out of our copending Indian Patent Application No. 67413.

We claim :

1. An electrolyte for the anodic oxidation of aluminium metal consisting essentially of an aqueous solution of sulfosalicylic acid and at least one substance selected from the group consisting of metal sulfates and sulfuric acid.

2. An electrolyte according to Claim 1 wherein said substance is ferric sulfate.

3. An electrolyte according to Claim 1 wherein said substance is sulfuric acid.

4. An electrolyte according to Claim 1 wherein the sulfosalicylic acid is present in amount of about 5 to 50% and said metal sulfate and/or sulfuric acid is present in an amount equivalent to not more than 15% by weight sulfuric acid.

5. An electrolyte according to Claim 4 wherein said metal sulfates and/or sulfuric acid is present in an amount equivalent to about 0.1 to 15% sulfuric acid.

6. An electrolyte according to Claim 1 wherein said sulfosalicylic acid is present in amount from about 7 to 15% and said metal sulfates and/or sulfuric acid is present in an amount equivalent to about 0.3 to 4% sulfuric acid.

7. An electrolyte according to Claim 5 wherein said substance is sulfuric acid.

8. An electrolyte according to Claim 6 wherein said substance is sulfuric acid.

9. An electrolyte according to Claim 2 wherein said sulfosalicyclic acid is present in amount of about 15% and said ferric sulfate is present in amount of about 5%.

10. Articles whenever treated with an electrolyte substantially as claimed in any one of the preceding Claims 1-9.

DEPENNING & DEPENNING,

Agents for the Applicants.

Dated this 27th day of December, 1960.

MGIP Basrk.—SL—37 Patent/61—26-3-62—100.

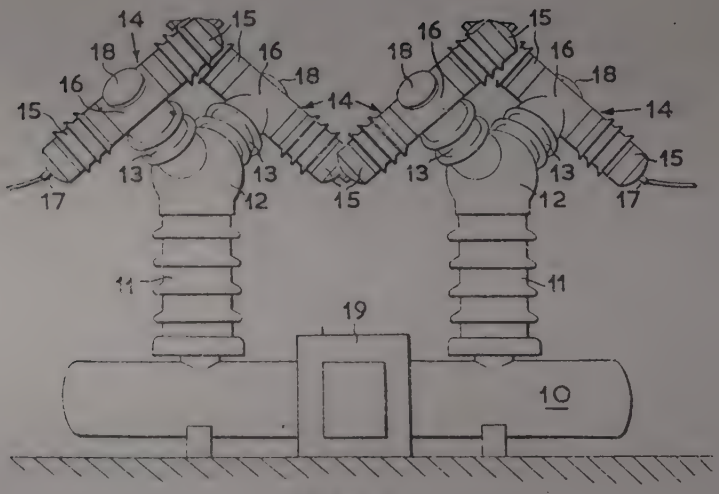

FIG. 1

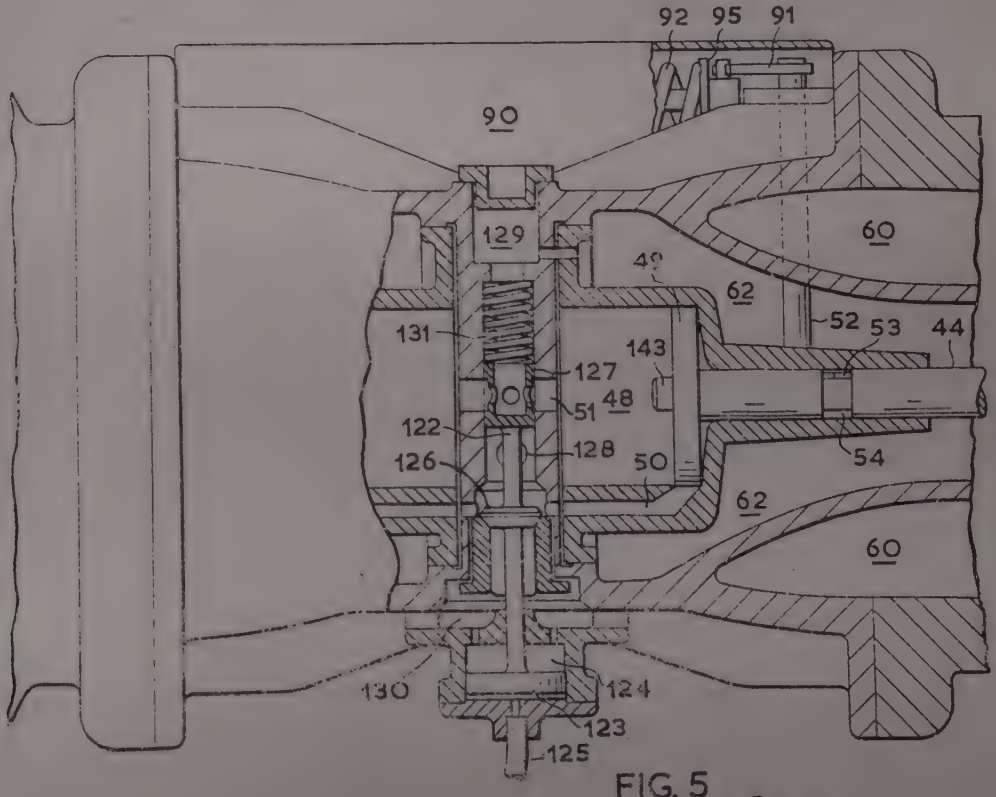

FIG. 5

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Figures 8 and 9 are respectively a vertical section and horizontal section of a portable kitchen mixer (with heaters not shown) the section plane of Figure 9 being indicated by the chain line 9a-9a of Figure 8, and that of Figure 8 by the line 8a-8a in Figure 9;

Figure 10 is a vertical section of another form of kitchen mixer;

Figures 11 and 12 are horizontal sections on chain lines 11a-11a,, 12a-12a respectively in Figure 10;

Figures 13 and 14 are views similar to Figures 1 and 2 of yet another kitchen appliance;

Figures 15 and 16 are respectively central vertical and horizontal sections of such parts of a drilling machine as concern the present invention, a small part of Figure 16 being seen in top plan, and Figure 17 being a scrap vertical section of part of the machine;

Figure 18 shows in perspective a duct structure;

Figures 19 and 20 are a partial horizontal section and vertical section respectively of a lawn mower;

Figures 21 and 22 are respectively a horizontal and vertical section of the rear of an automobile, and

Figure 23 is a vertical section of the rear of another form of automobile.

Referring to the drawings, Figures 1 and 2 show a power unit according to the invention for a kitchen appliance. An electric motor 1 and blower 2 are accommodated in a common housing 3, which has inlet and outlet apertures designated 4, 5 respectively 6 for cooling air. The blower 2 has a cylindrical bladed rotor which is closed at its ends and traversed twice by the cooling air in a direction transverse to the rotor axis. A very suitable form of blower is described in United States patent No 2942773. Further forms of blower are shown in British patent specification No. 876611. The housing 3 is mounted by means of rings 7 and 8 respectively of rubber or similar elastic material in such a manner as to be physically insulated against transmission of noise to the wall 6 of the appliance. The mounting with acoustic insulation can of course also be effected in various alternative ways known per se. The space formed between the housing 3 and the wall 6 is constructed as a resonator for the air passing through. An inlet air passage 10 is connected to the inlet aperture 4 and an outlet air passage 11 to the outlet aperture 5 of the housing 3. The two air passages 10 and 11 respectively are lined with sound-absorbing material 12.

Figures 3 and 4 show another embodiment of the invention. An electric motor 13 and a blower 14 similar to the blower 2 of Figures 1 and 2 are disposed in a common housing 15. Inlet apertures, 16, 17 and 18 for entry of the cooling air to the interior of the housing are here constructed in the form of nozzles which blow the cooling air preferentially to those parts of the motor which become particularly hot. The housing 15 is mounted in an enclosing wall 19 of the apparatus by means of rings 20 and 21 respectively of rubber or other elastomeric material in such a manner as to be physically insulated against the transmission of noise to the wall 19. An inlet air passage 23 is connected to the inlet aperture 22 of the space formed between the housing 15 and the wall 19. An outlet air passage 25 is similarly connected to the outlet aperture 24 of the housing 15. The two air passages have a common wall 26 which consists of a thin non rigid foil of a plastics material. Above the two air passages there are disposed resonators 27 and 28 respectively of different sizes; a multiplicity of apertures 29 which have different depths are formed in a wall dividing the resonator 27, 28 from the air passages 24, 25. This arrangement permits the filtering out of a wide band of acoustic frequency from the air passing through the air passages.

Figures 5, 6 and 7 illustrate a power unit according to the invention for a kitchen machine; of this machine only a plate 31 forming part of a work table of the machine is shown, the power unit being suspended therefrom by a flange 30. The shaft 33 of an electric motor 32 drives a pair of shafts 35 by means of V-belts 34, these shafts 35 being intended for driving devices (not shown) mounted on the work table. A blower 36 similar to that of Figures 1 and 2 is mounted with the motor 32 within a common housing 30. This blower induces a flow of cooling air through an inlet air passage 37, through an inlet aperture 38 of the housing 30, through the motor 32, the blower rotor 36, an outlet aperture 40 of the housing 39, and an outlet air passage 41. Between the inlet air passage 36 and the outlet air passage 41 are disposed two resonators 42 and 43 which have apertures 44 and 45 to the inlet and outlet passages respectively. In order to prevent equalization of pressure between the inlet and outlet air passages, these apertures 44 and 45 are covered with foils 46 and 47 respectively. Thus while the resonators 42, 43 are associated acoustically with the inlet and outlet passages they are closed against entry and cooling air The walls of the resonators 42, 43 consist of sound-absorbing materials. By means of this arrangement the absorption of sound both in the inlet air passage and in the outlet air passage through the same resonators is permitted while the foils 46 and 47 respectively protect the interior of the resonator from becoming soiled by dirt entrained with the cooling air.

Figures 8 and 9 show a hand-held kitchen mixer provided with a power unit according to the invention. An electric motor 48 and blower 49 are accommodated in a common housing 50, which has inlet apertures 51 and outlet apertures 52 for cooling air. In this embodiment of the invention the blower is of the radial type i.e., air enters axially the interior of a cylindrical bladed rotor closed at one end only and is discharged radially thereby. An inlet air passage 53 with openings 54 to the exterior is connected to the inlet apertures 51, and is constructed as a resonator space. Though not shown the walls of the resonator can be made of sound-absorbing material. Moreover, the space defined between the motor wall and the housing 50 is also a resonator. An outlet air passage 55 communicates through openings 56 to the exterior and is connected to the outlet aperture 52 of the housing 50. The motor shaft 57 drives a worm 58 meshing with gearwheels 59 and 60 which in turn operate the drive shafts 61 and 62 respectively for the stirring mechanisms. A handle 63 is provided on the common housing of the apparatus.

Figures 10, 11 and 12 illustrate another form of portable kitchen mixer incorporating a power unit according to the invention. An electric motor 64 and a blower 65 such as that of Figures 1 and 2 are mounted in a common housing 66 providing inlet apertures 67 and outlet apertures 68 for the cooling air.

An inlet air passage 69 conected to the inlet aperture 67 and an outlet air passage 70 connected to the outlet aperture 68 are provided within the handle 71 of the apparatus; these passages 69, 70 run side by side and are separated by a partition 72. As in the previously described embodiment the motor drives the drive shafts for the stirring mechanism through a shaft, worm and gearwheels.

Figures 13 and 14 illustrate a portion of a kitchen appliance, for example a table-mounted mixer, provided with a power unit according to the invention. An electric motor 73 and a blower 74 which is similar to that of Figures 1 and 2 are disposed in a common housing 75 which has inlet apertures 76 and outlet apertures 77 for the cooling air. The air passages 78 and 79 connected to the said apertures are in this case formed by the space existing between the housing 75 and an enclosing wall 80 of the apparatus which space is divided into two halves by a partition 81. The wall 80 of the apparatus contains at its base inlet nozzles 82 for the cooling air and at its oppositely situated upper part an outlet slot 83. The motor shaft 84 can be made to drive any desired kitchen apparatus.

Figures 15, 16 and 17 illustrate a portable drilling machine with a power unit according to the invention An electric motor 120 and a blower 121 as in Figures 1 and 2 are disposed in a common housing 122, which has an inlet aperture 123 and an outlet aperture 124 for the cooling air. The housing 122 is mounted on the enclosing wall 127 of the apparatus by means of rings 125 and 126 of rubber or similar elastomeric material such as to be physically insulated against noise transmission from the housing to said wall. The apparatus is provided with handles 128 and 129 accommodating an

inlet air passage 130 and an outlet air passage 131 respectively. These two air passages 130, 131 are constructed as soundabsorbing passages: their walls have a large number of holes 131a and define with the handles 128 and 129 an annular space filled with sound-absorbing material 132. The shaft 133 of the motor leads to the gearing of the apparatus. The inner ends of the handles 128 and 129 are formed with slots 134 and surrounded by rings 135 having corresponding slots 136. In the normal position of the rings the slots 134 and the slots 136 are out of register. Bi-metal strips 137 are fastened to the housing 122 and rigidly connected to the rings 135 by means of pins 138 which pass through slots 139 in the wall 127 of the apparatus. When the bi-metal strips are tensed in consequence of heating above a given temperature, the rings 135 are rotated upon the handles 128 and 129 so that the slots 134 coincide with the slots 136. Air then passes into and out of the apparatus through the slots 134 and 136 with slight air resistance. The power required by the motor is thus reduced, but the noise increases.

In a power unit according to the invention outlet air passage connected to the outlet aperture of the housing enclosing the motor and blower can consist of a large number of parallel bores in a sound-absorbing body, as illustrated in Figure 18. In the sound-absorbing body 85, which for example may consist of wadding, foam material, foam rubber, glass wool or slag wool, bores 86 for the cooling air are provided. These bores are stiffened by means of coil springs 87, which extend over the entire length of the bores and bear against their inner walls.

Figures 19 and 20 show a lawn mower with a power unit according to the invention. The power unit is situated within enclosing walls 89 and supported on wheels 88 and on which is secured a handle 90. The motor 91 is in this case a vertical-crankshaft internal combustion engine and drives a radial blower 92 situated above it. The engine and blower are disposed in a common housing 93 with an inlet aperture 94 and an outlet aperture 95 for the cooling air. The space formed between the housing 93 and the wall 89 of the apparatus is divided by a partition 96 into two resonator spaces 97 and 98 respectively, which can be lined with sound-absorbing material. An inlet air passage 99 leads into the resonator 98, and the outlet air passage 100 to the resonator 97. The two air passages are acoustically adapted in the resonators and made curved in order to damp the sound further. The outlet aperture 101 of the exhaust muffler 102 of the engine also leads into the resonator 98. The shaft 103 of the engine projects downwardly to drive the cutting blades 104 of the lawn mower.

Figures 21 and 22 illustrate a power unit according to the invention accommodated in the rear of an automobile. An internal combustion engine 105 drives a radial blower 106 and the driving axle 107 for the wheels 108 of the vehicle. A housing 109 encloses the engine and blower and forms a resonator 110 with an inlet aperture 111 and an outlet aperture 112 for the cooling air. Between the housing 109 and the walls 113 of the vehicle another resonator space 114 is formed. The vehicle 113 has apertures 115, from which a large number of inlet air passages 116 lead into the interior of the resonator 114. Between the bottom walls of the resonator 114, housing 109, and bottom 117 of the vehicle another resonator space 118 is formed. From this resonator space a large number of outlet air passage 119 lead into the atmosphere. For the purpose of further sound-damping, these passages are made curved.

Figure 23 also illustrates the arrangement of a power unit according to the invention in the rear of an automobile. The engine 140 and blower 141 (which is similar in operation to that of Figures 1 and 2) are disposed in common housing 142, which has an inlet aperture 143 and outlet aperture 144 for the cooling air. The engine drives the blower and the driving axle 145 for the wheels 146 of the vehicle. The inlet air passage 147 and outlet air passage 148 are disposed in the space formed between the housing 142 and the wall 149 of the vehicle. The walls of the passages 147, 148 are lined with sound-absorbing material. In order to relieve the engine, the cooling air can be discharged to the atmosphere through an aperture 151 adapted to be closed by means of a flap 150, without having to flow through the outlet air passage 148. A similar aperture with a flap can be disposed between the inlet air passage 147 and the housing opening 143.

We claim:

1. A power unit comprising a motor having at least one power output shaft, and a blower driven from said shaft to provide cooling air for the motor, wherein a housing surrounds the motor and provides an inlet aperture and an outlet aperture the housing being otherwise closed, at least one air duct is connected to the inlet, at least one air duct is connected to the outlet, said ducts communicating with the motor and blower whereby said blower induces air flow from inlet to outlet duct through the motor, and sound-absorbing means is associated acoustically with said ducts.

2. A power unit as claimed in Claim 1, wherein said blower includes a cylindrical bladed rotor closed at its ends through which the throughput of the blower is conveyed twice in a general direction transverse to the rotor axis.

3. A power unit as claimed in Claim 1 or in Claim 2, wherein the inlet and outlet ducts have a common separating wall constituted by a foil.

4. A power unit as claimed in any of Claims 1 to 3, wherein said sound-absorbing means includes at least one resonator disposed on a wall of one of said ducts.

5. A power unit as claimed in Claim 4, wherein said resonator or resonators communicate acoustically with the interior of the duct through a foil.

6. A power unit as claimed in Claim 4 or in Claim 5, wherein said resonator or each said resonator defines a space lined with sound absorbing material.

7. A power unit as claimed in Claim 4, wherein said resonator or each said resonator comprises walls formed of sound-absorbing material protected against cooling air with an outer foil layer.

8. A power unit as claimed in any of Claims 4 to 7, wherein said motor and said housing define between them a space forming or containing said resonator or resonators.

9. An appliance incorporating a power unit as claimed in Claim 8, said appliance providing outer walls defining with said housing said inlet and outlet ducts.

10. An appliance comprising a power unit as claimed in any of Claims 1 to 8 and a pair of hollow open-ended handles said inlet and outlet ducts passing through said handles.

11. A power unit as claimed in any of the preceding claims, wherein said housing comprises normally closed flaps which are openable to provide communication between said motor and the exterior by-passing said inlet and outlet ducts.

12. A power unit as claimed in Claim 11, wherein a thermostat is provided to control the opening of said flaps.

13. A power unit as claimed in Claim 1 or in Claim 2, including a sound-absorbing body providing a multiplicity of parallel channels which form inlet and outlet ducts said body providing also the soundabsorbing means located in said ducts.

14. A power unit as claimed in Claim 13, including a plurality of coil springs located in said body and stiffening the walls of the channels therein.

15. A power unit as claimed in any of the preceding claims, wherein the mouths of the ducts towards the exterior are formed as nozzles.

16. A power unit as claimed in any of the preceding claims, wherein said motor is an internal combustion engine exhausting to said outlet.

17. A power unit or appliance as claimed in any of the preceding claims, wherein the motor is supported in the housing by means which insulate the latter at least in part against noise generated in the motor.

18. A power unit or appliance as claimed in any of Calims 1 to 16, including a support outside the housing, wherein the motor is rigidly fixed to the housing and

the housing is carried on the support by means which insulate the latter at least in part against noise generated in the motor.

19. A power unit or appliance as claimed in either of Claims 17 and 18, wherein said sound insulating support means consist of a pair of rubber rings.

20. The kitchen appliance herein described with reference to Figures 1 and 2 of the accompanying drawing.

21. The kitchen appliance herein described with reference to Figures 3 and 4 of the accompanying drawing.

22. The kitchen appliance herein described with reference to Figures 5 to 7 of the accompanying drawing.

23. The kitchen appliance herein described with reference to Figures 8 and 9 of the accompanying drawing.

24. The kitchen appliance herein described with reference to Figures 10 to 12 of the accompanying drawing.

25. The kitchen appliance herein described with reference to Figures 13 and 14 of the accompanying drawing.

26. The drilling machine herein described with reference to Figures 15 to 17 of the accompanying drawing.

27. The lawn mower herein described with reference to Figures 19 and 20 of the accompanying drawing.

28. The automobile herein described with reference to Figures 21 and 22 of the accompanying drawing.

29. The automobile herein described with reference to Figure 23 of the accompanying drawing.

B. DuPENNING

OF DuPENNING & DuPENNING,

Agent for the Applicants.

Dated this 27th day of December 1960.

M.G.D.C.—L—104 Patent/62—9-5-63—100.

Firth Cleveland Ltd.

No. 74700.

3 Sheets.
Sheet 1.

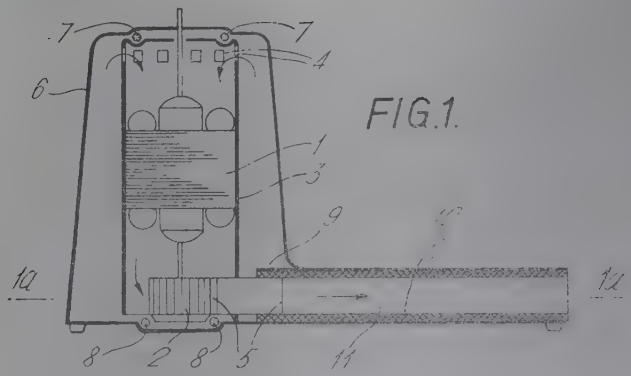

FIG.1.

FIG.2.

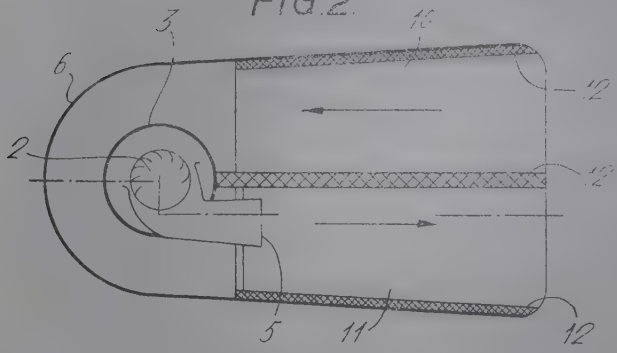

FIG.3.

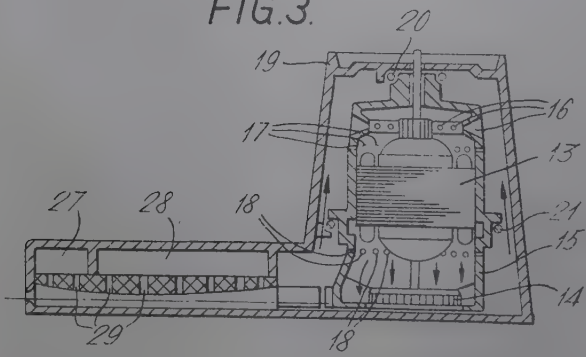

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FIG.4.

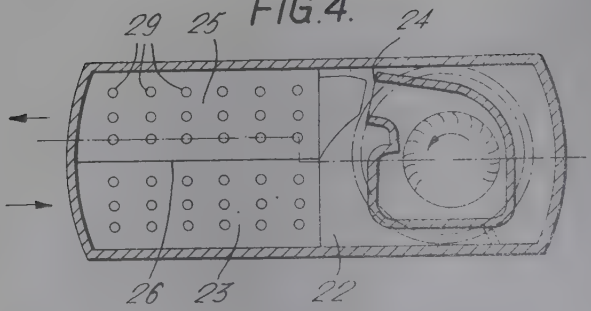
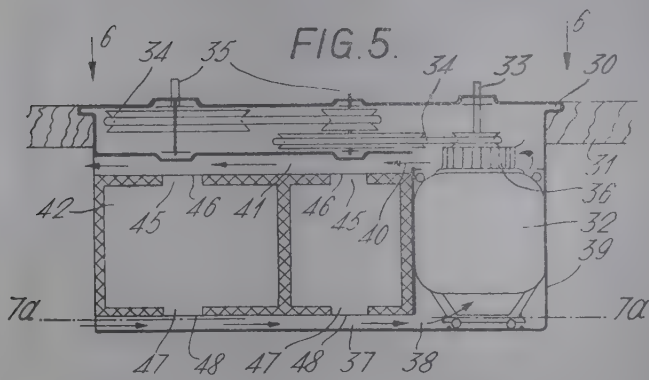


FIG.5.



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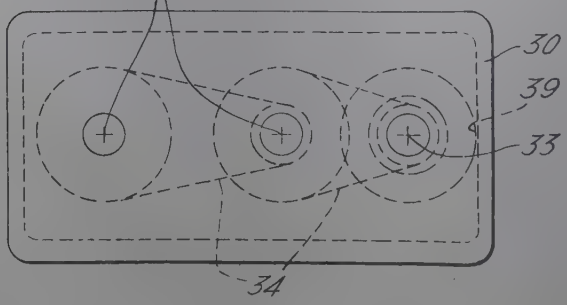

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FIG.7.

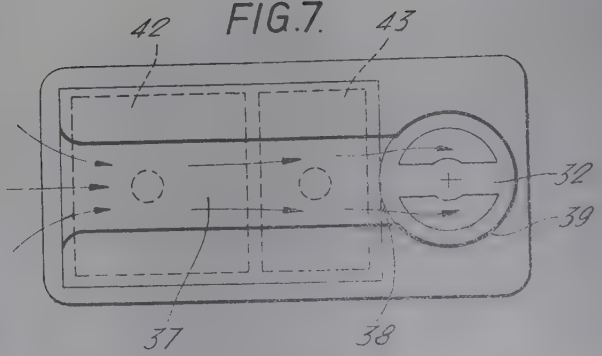

FIG.8.

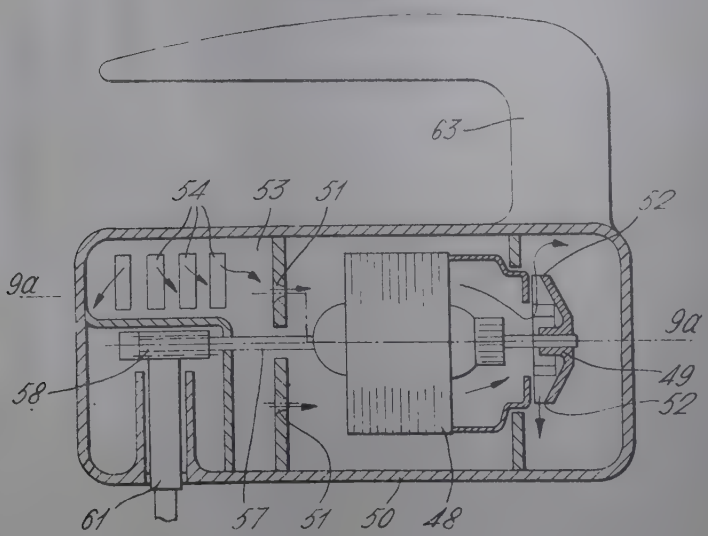

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FIG.9.

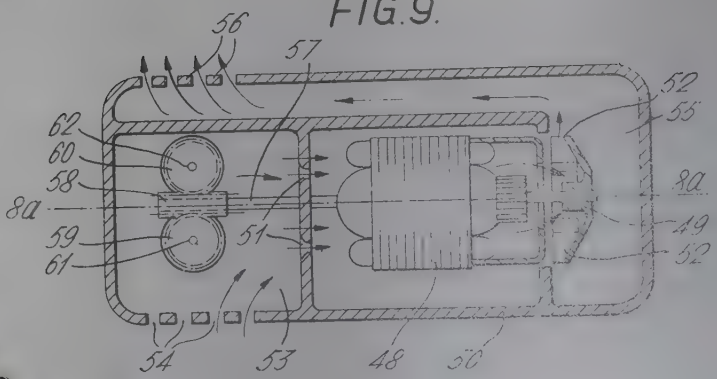

FIG.10.

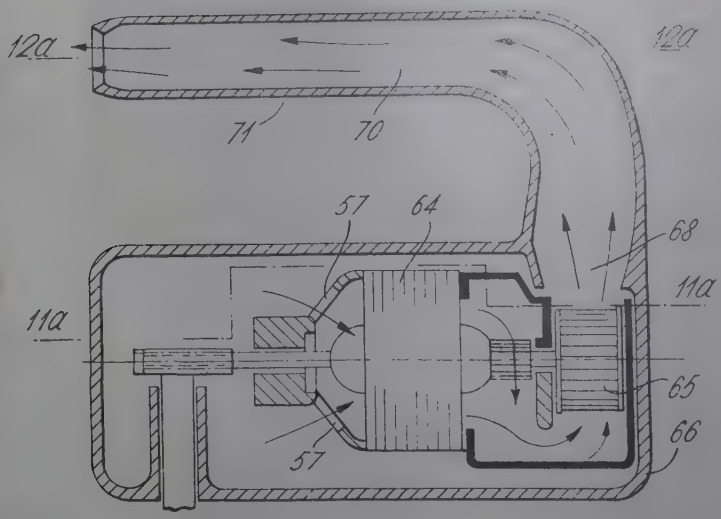

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FIG.11.

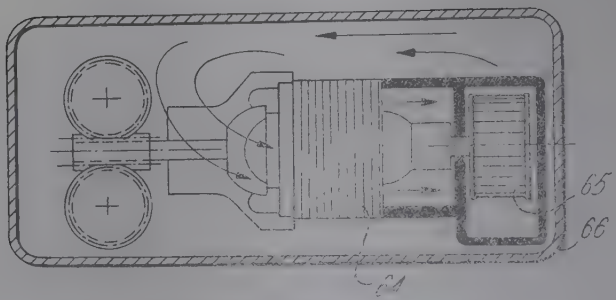

FIG.12.

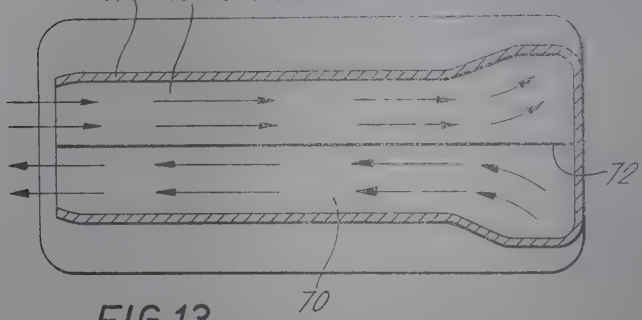

FIG.13.

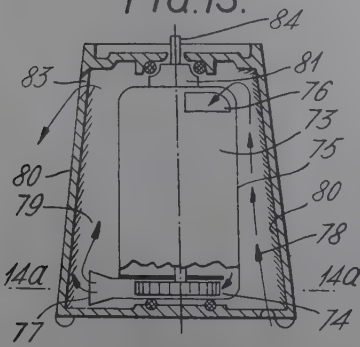

FIG.14.

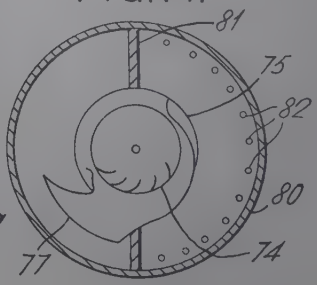

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FIG.15.

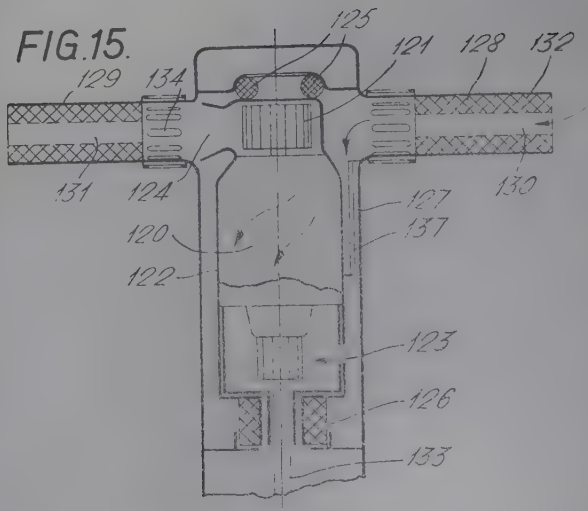

FIG.16.

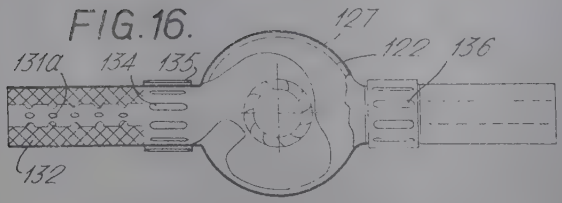

FIG.17.

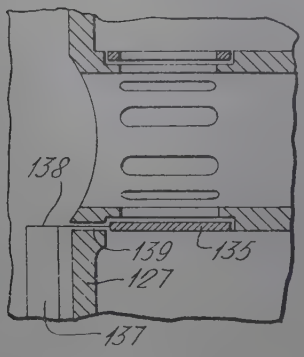

FIG.18.

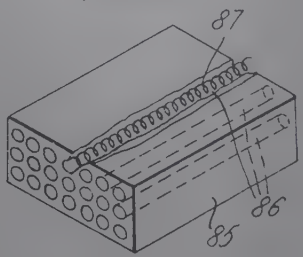

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FIG.19.

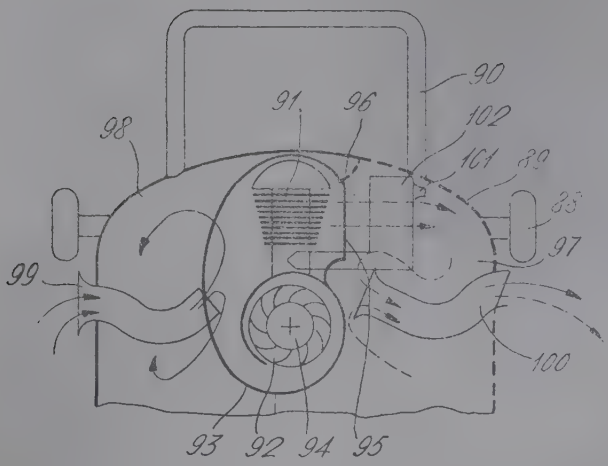

FIG.20.

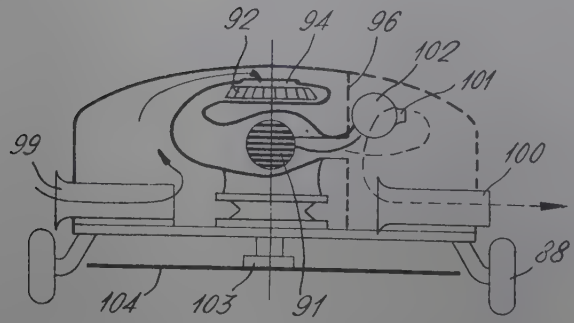

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FIG. 21.

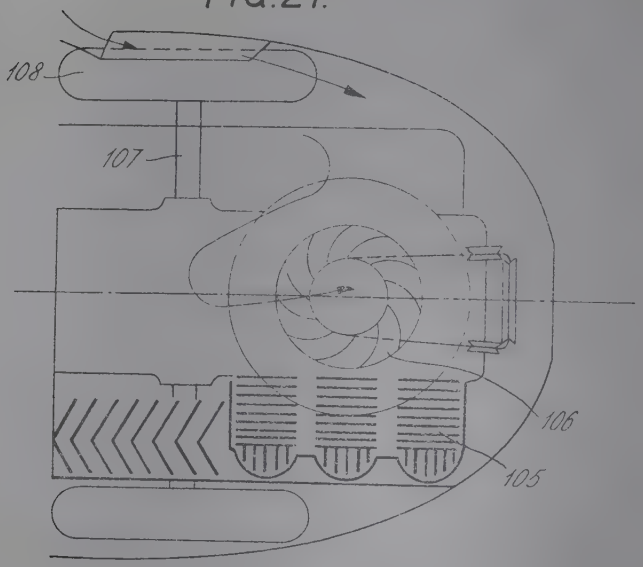

FIG. 22.

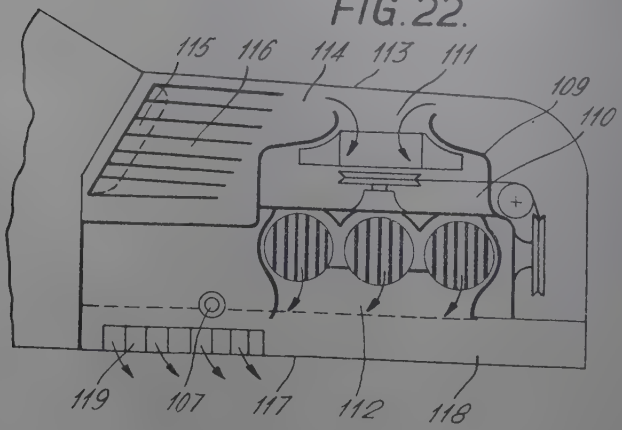

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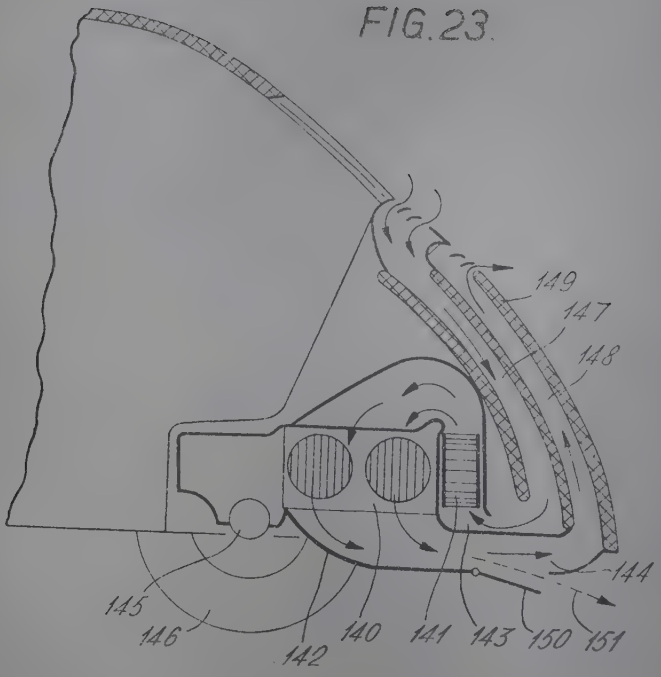
FIG. 23.



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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17

Specification No. 74701, filed 27th December 1960. Reciprocity date United Kingdom 15th December 1960. (Accepted 16th January 1967.)

"IMPROVEMENTS RELATING TO A SCRAP PACKAGING PRESS."

WALDEMAR LINDEMANN, a German citizen, of Erkrather Strasse 401, Duesseldorf, Germany.

The following Specification particularly describes and ascertains the nature of this Invention and the manner in which it is to be performed :—

This invention relates to a scrap packaging press having a press box which can be closed by a hinged cover and a trough which is provided with a filling plunger and of which the mouth opens above one side wall of the press box and is situated in the same plane as one side edge of the hinged cover, the plunger being flush with the bottom and the side walls of the trough. Presses of this kind can be operated at high speeds, because the trough can be filled when the cover is closed and while the package of scrap is being formed in the press box. The hinged cover has the advantage that the press box is accessible from the top and if the wall of the press box opposite the mouth of the trough is extended upwardly, a space which increases the volume of the trough is obtained, so that pieces of scrap which are longer than the trough can be dealt with by the press.

In order to prevent pieces of scrap being jammed between the front edge of the cover and the opposite wall of the press box when the cover is being closed, it is usual to arrange at the level of the mouth of the trough a wall having a cylindrical guide surface concentric with the axis of the cover for guiding the front edge of the cover. In this case it is advantageous to provide this surface with grooves in which corresponding teeth on the front edge of the cover engage. Owing to the wall on which the cylindrical grooved or ungrooved guide surface is formed, difficulties, however, occur at the mouth of the trough. Thus, the mouth of the trough may only be made so wide that no restriction of the cross-section occurs at the mouth, that is to say the scrap pushed forwards by the plunger does not meet an obstruction anywhere when the cover is open. Then, however, as shown in the drawings, there is formed in the plane of the mouth of the trough a wall suface along which one side edge of the cover slides. Pieces of scrap may become jammed between the cover and this surface, particularly at the corner which it forms with the bottom of the mouth of the trough. The cover cannot then be completely closed and the pieces of scrap at the place in question must be removed by hand or with a crane before the work can proceed. It may even happen that the cover becomes jammed to such an extent that it becomes immovable and parts of the press must be dismantled in order to remove the obstacle.

In the know presses of the above-mentioned kind, the cross-section of the trough is rectangular. In order to obviate the disadvantage mentioned, in the press of the invention this rectangular shape is given up and, in accordance with the invention, the lower end of the front edge of the side wall of the through remote from the axis of the cover lies in the cylindrical guide surface and also this side wall, viewed in the direction of the plunger, runs in such a way that it nowhere recedes behind the guide surface. In this way the dangerous corner is eliminated. At the same time one side wall of the trough is no longer vertical and the same applies to the side surface of the plunger which moves along this wall.

The theoretically ideal form of the side wall of the trough remote from the axis of the cover would be a lateral continuation of the cylindrical guide surface so that it would be cylindrical over its entire length, in which case the plunger must then have a correspondingly curved form. The cost of this would not, in general, be worthwhile, because a relatively rough approximation of the theoretically ideal form is sufficient to fulfil this requirement in practice. This approximation consists in forming the side wall of the trough remote from the axis of the cover from one or more plane pieces which are inclined to the vertical. A particularly good approximation to the ideal form is obtained if the front edge of the side wall of the trough remote from the axis of the cover constitutes one or more chords of the circular arc which forms the one side edge of the cylindrical guide surface.

An embodiment of the invention is illustrated, by way of example, in the accompanying drawings, in which

Fig. 1 is a perspective view with the side wall of the press box partly broken away and the hinged cover omitted ;

Fig. 2 is a plan of the press shown of Fig. 1, viewed from above ;

Fig. 3 is a section on the line A-B of Fig. 2 with the cover open ;

Fig. 4 is a section on the line A-B of Fig. 2 with the cover closed ;

Fig. 5 is a section on the line C-D of Fig. 2, and

Fig. 6 is a section on the line E-F of Fig. 2.

Referring to the drawings, all essential element of the press can be seen in Fig. 1 with the exception of the hinged cover. The press box is in the form of a rectangle and is enclosed by three fixed and three movable walls. The bottom 11 and the side walls 12 and 13 form the fixed walls, a press plunger 14, a door 15 and a hinged cover 16, which is shown in Figs. 3 and 4, form the movable walls. The hydraulic drive 17 for the plunger 14 is shown in Figs. 3 and 4. A door 15 can be moved out of the position illustrated by a driving means, which is not illustrated, so that the package formed in the press box can be pushed by means of the plunger 14 out of the opening 18. The hinged cover 16 can swing about an axis 19. Its hydraulic driving means is linked to a pivot 20 by means of a push rod acting in the direction of the arrow P shown in Figs. 3 and 4.

Above the press box 10 there is a trough 21 which is open on top and has a bottom 22 and side walls 23 and 24. A filling plunger 25 is movable in the trough 21 and is driven by a hydraulic drive 26 which is shown in Fig. 6. The plunger is flush with the bottom surface 22 and with the side walls. The upper edge of the plunger is guided by a ledge-like extension 27 of the side wall 24. The mouth of the trough 21 is situated in the same plane as one side edge 28 of the hinged cover 16. The edge 29 which with the side wall 13 of the press box 10 forms part of the bottom surface of the trough can be equipped with cutters 30, and the edge 28 of the cover 16 which moves past this edge can also have a cutting reinforcement 30a which is shown in Fig. 2. Small pieces of scrap which get jammed between the cover and the bottom edge of the trough can be cut by means of these cutting edges.

In operation of the press, scrap is charged by a magnetic crane into the trough 21, the plunger 25 being retracted and

the cover 26 being open ; scrap is also thrown into the press box 10. The scrap in the trough is pushed by the plunger 25 into the press box 10 while the cover is open. Pieces of scrap which extend beyond the width of the press box 10 are bent together between the plunger 25 and an upward extension 12a of the side wall 12 and brought to a length such that they fit into the press box. When the press box 10 has been filled with an amount of scrap sufficient for making a package of reasonable size, the cover 16 is brought to the closed position shown in Fig. 4, the scrap being thereby compacted for the first time. After this, the plunger 14 is moved forwards in order to complete the packaging. The door 15 is then opened and the bundle of scrap is ejected by the plunger 14 through the opening 18.

In order to prevent projecting parts of scrap from interfering with the closing of the cover 16, a wall 32 is arranged opposite the end face 31 of the cover, and a cylindrical guide surface 33 concentric with the axis 19 of the cover is formed on the wall 32 for the end face 31 of the cover. This cylindrical surface can be provided with grooves 34 which form teeth, in which teeth 34a on the end face 31 of the cover 16 engage when the cover is closed. These teeth on the cover, together with those on the wall opposite it, prevent the pieces of scrap being jammed between these two parts.

The lower end point 36 of the front edge 35 of the side surface 24 which is situated in the plane of the mouth of the trough lies, as shown in Figs. 1 and 3, in the cylindrical surface 33. In this there is a considerable difference as compared with the usual form, in which the edge of the side surface 24 is vertical, as shown by the dash dot straight line 37 in Fig. 1 which intersects the front edge 29 of the the bottom surface 22 at the point 38 through which the lower edge 39 of the side surface 24 also passes as shown by the dash-dot line. There is then formed a surface 40 which is bounded by two straight lines and a circular arc and gives rise to the jamming of the scrap between the cover and the one side wall of the trough. In particular, the corner at the point 38 forms a place where pieces of scrap collect which hold up the cover and cause it to become jammed.

These disavantages are avodided by disposing the lower end point 36 of the front edge of the surface 24 in the surface 33 and particularly good results are obtained by making the edge 35 a chord of the circular arc 41 which forms the side of the cylindrical guide surface 33. Then, the upper end point 42 of the front edge 35 of the side surface 24 also lies on the circular arc 31, as shown in Figs. 1 and 3. Between the points 36 and 42 a narrow circular segment always does exist. This small segment between the side surface of the cover and the side surface of the trough gives rise to no appreciable trouble as has been found in practice. It is not necessary, therefore, to arranged the points 36 and 42 with mathematical accuracy.

For explaining the invention the simple case has been selected in which the scrap to be formed into a package is subjected only to two pressing pressures, namely the pressure of the cover 16 and the pressure of the plunger 14. Frequently, by arranging a further plunger movable transversely to the plunger 14, a further pressure can be employed in order to increase the compacting. This, however, is of no consequence to the invention.

It is also of no importance for the invention whether the front side of the cover is toothed in the manner illustrated. Even if, for facilitating the construction, these teeth are omitted, the invention retains its importance.

If the height of the trough 41 in relation to the height of the press box is made considerably greater than in the constructional example illustrated, the width of the segment 33 can, in some cases, become so great that jamming is possible. Then, to lessen this possibility the front edge of the side surface 24 of the trough can be divided into two or more chords of the circular arc 41, the surface 24 and the side surface of the plunger 25 adjacent to it also being formed of plane pieces arranged at an angle one to the other.

I CLAIM :—

1. A scrap packaging press comprising a press box, a hinged cover by which the press box can be closed, a charging trough the mouth of which opens above one side wall of the press box and is situated in the same plane as the hinged cover, a charging plunger flush with the botton and side walls of the trough, and with a wall arranged on a level with the trough having a cylindrical guide surface for the front edge of the cover concentric with the axis of the cover, wherein the lower end point of the front edge of the trough side wall remote from the axis of the cover lies in the cylindrical guide surface and said side wall runs in such a manner that, viewed in the direction of the plunger, it nowhere recedes behind the guide surface.

2. A press according to claim 1, in which the side wall of the trough remote from the cover and the side surface of the plunger adjacent this side wall consist of one or more plane pieces inclined to the vertical.

3. A press according to claim 2, in which the front edge of the trough remote from the axis of the cover forms one or more chords of the circular arc which bounds the cylindrial guide surface.

4. A scrap packaging press substantially as described with reference to the accompanying drawings.

G. S. DAVAR
of L. S. DAVAR & Co.
Applicants' Attorney.

Dated this 27th day of December 1960.

Printed by The Nolys Printing Works, Calcutta-1.

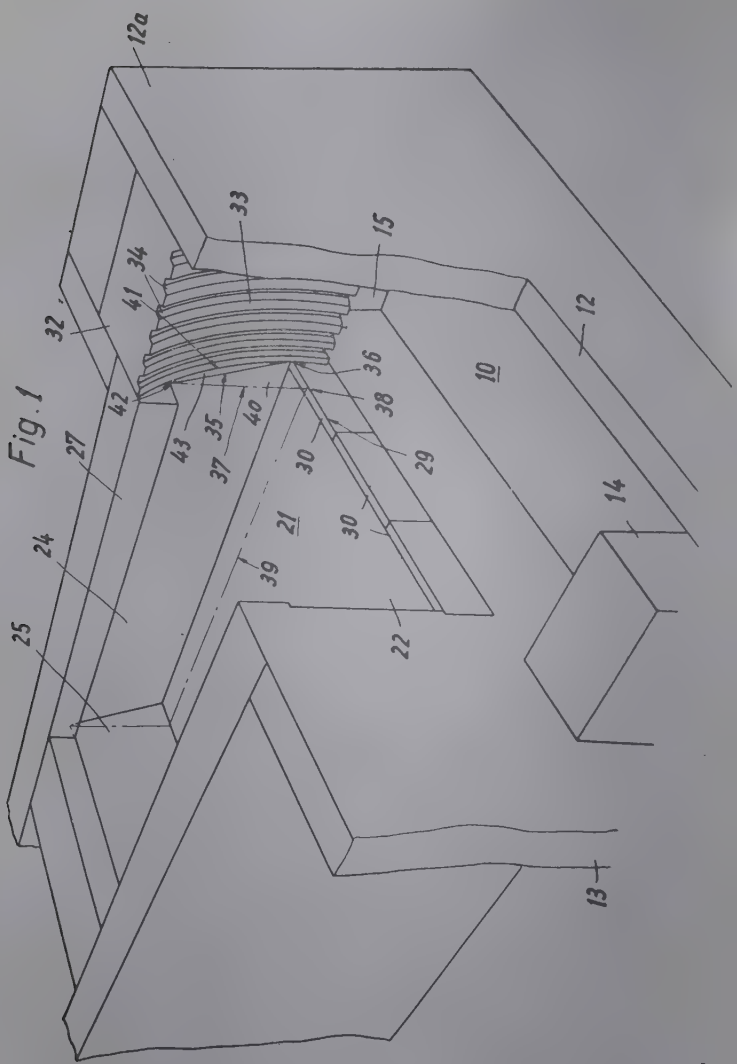

Fig. 1

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of L. S. DAVAR & CO.
APPLICANT'S ATTORNEY.

No. 74701 of 1960.

NAME: WALDEMAR LINDEMANN.

SIX SHEETS

SHEET NO. 2

Fig. 2

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APPLICANT'S ATTORNEY.

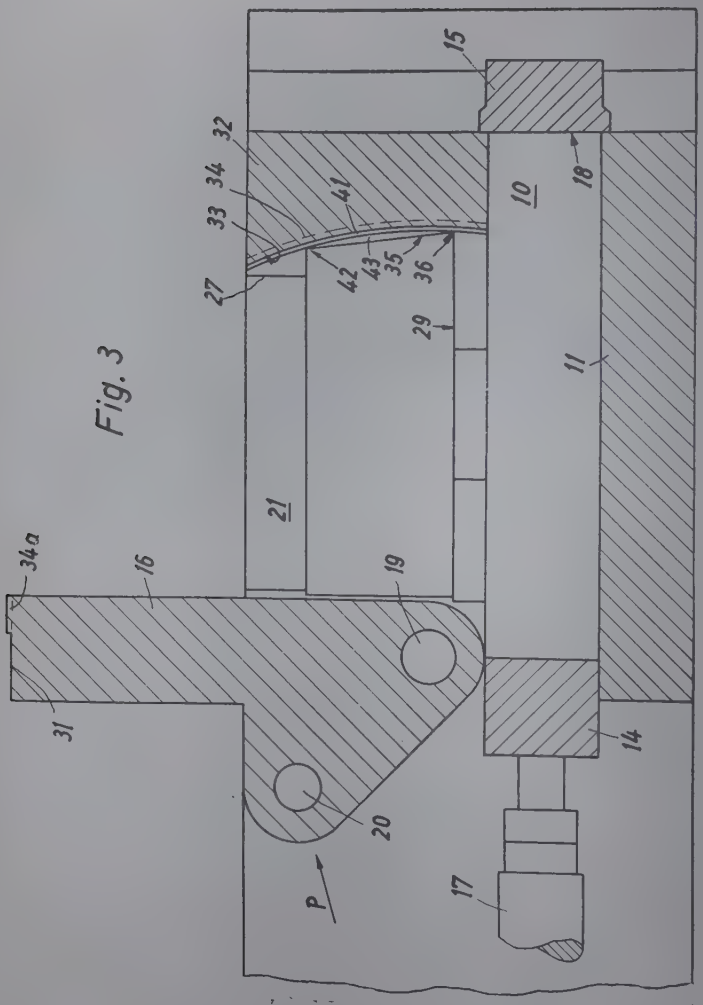

Fig. 3

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of L. S. DAVAR & CO.
APPLICANT'S ATTORNEY.

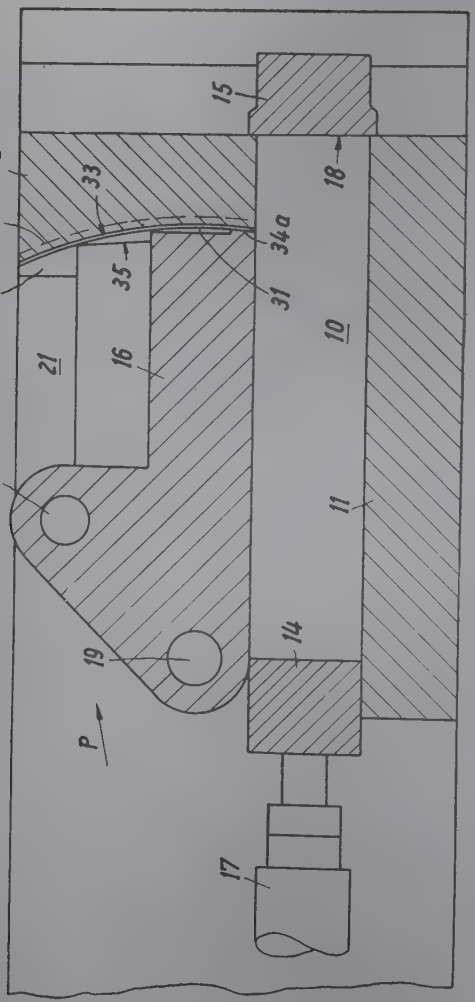
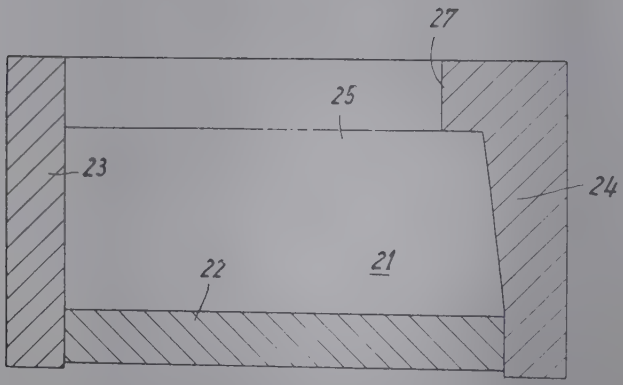


Fig. 4

G. S. DAVAR
of L. S. DAVAR & CO.
APPLICANT'S ATTORNEY.

Fig. 5



G. S. DAVAR
of L. S. DAVAR & CO.
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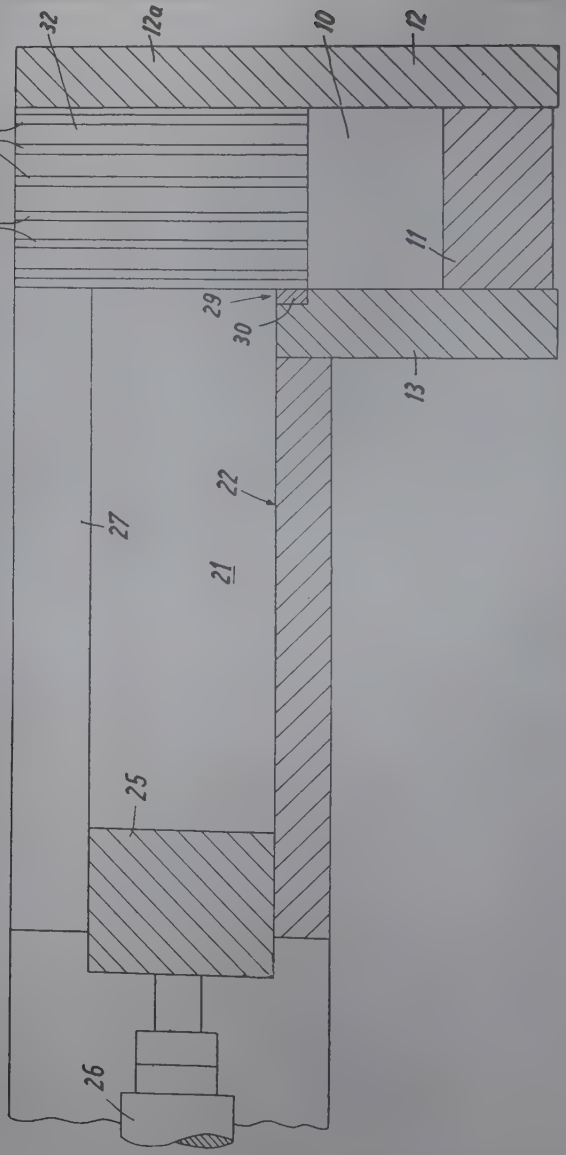

Fig. 6

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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74705, 28th December 1960. (Accepted 9th May 1962.)

PROCESS FOR THE PRODUCTION OF HYDROCHLOROTHIAZIDE.

THE BRAHMACHARI RESEARCH INSTITUTE, 82/3, Cornwallis Street, Calcutta-4, West Bengal, India, An Indian Registered Partnership Firm whose partners are Dr. Phanindra Nath Brahmachari and Dr. Nirmal Kumar Brahmachari, both Indian citizens of the same address.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

The present invention relates to an improved process for the manufacture of Hydrochlorothiazide and more particularly, to the production of 6-chloro-7-sulphamyl-3 : 4-dihydro-1 : 2 : 4 - benzthiadiazine - 1 : 1 - dioxide of the formula shown in Figure 1 of the accompanying drawings.

The compound of this invention is a therapeutically useful agent as it exhibits an excellent diuretic and saluretic actions ; specially increased excretion in the urine of the chloride is favourable.

There are various processes known in the chemical art for preparing benzthiadiazine derivatives. The preparation of 6-chloro-7-sulphonamido-benzdihydro-1 : 2 : 4-benzthiadiazine-1 : 1-dioxide has been reported earlier in Indian Patent Specification No. 68073. According to the said prior patent, the process comprises reacting 3-halo-4 : 6-disulphonamido aniline with an aldehyde of the formula R-CHO where R stands for hydrogen, an alkyl or halogenated alkyl radical.

The investigators of the present invention have, however, observed that with certain modifications, the above cited process can be carried out more effectively, conveniently and continuously without in any way impairing the yield and purity of the end product. On the other hand, the modifications suggested in the present invention aims at producing an end product with higher yield and purity than has hitherto been possible in the known art. The modification essentially consists in incorporating to the reactants a catalytic amount of ammonium chloride.

Accordingly, this invention provides a process for the manufacture of 6-chloro-7-sulphamyl-3 : 4-dihydro-1 : 2 : 4-benzothiadiazine-1 : 1-dioxide of formula shown in Figure 1 of the accompanying drawings which comprises reacting 4-amino - 6 - chloro - 1 : 3 - benzenedisulphonamide of the formula shown in Figure 2 of the accompanying drawings with formalin characterised in that the reaction is conducted in the presence of ammonium chloride in aqueous medium. Advantageously, the reaction is carried out at 125° to 130°C.

The above reaction takes place very smoothly in a relatively short period of time thereby yielding a higher amount of pure end product. Another usefulness of the present process is that due to the aforesaid advantages, the product can be conveniently produced on a commercial scale.

The following illustrates an example of one embodiment of this invention and the manner in which it is performed.

Example

In a 250 ml. round-bottomed flask fitted with a reflux condenser and a dropping funnel are placed 8 g. of 4-amino-6-chloro-benzenedisulphonamide and 13 cc. water; the mixture is heated in an oil bath to boiling point. At this point a solution of 2·5 cc. formalin and 1·6 g. of NH_4Cl in 3 cc. of water is added slowly through the dropping funnel. The solution is then refluxed for about 2 hours, the temperature of the oil bath being kept at 125-130°C. The resulting mixture is cooled, filtered and the precipitate is washed with cold water. The product is recrystallised from water. (M.P. 269 to 270°C. Yield — 7 g.).

We claim :

1. A process for the manufacture of 6-chloro-7-sulphamyl-3 : 4-dihydro-1 : 2 : 4-benzothiadiazine - 1 : 1 - dioxide of formula shown in Figure 1 of the accompanying drawings which comprises reacting 4-amino-6-chloro-1 : 3-benzenedisulphonamide of the formula shown in Figure 2 of the accompanying drawings with formalin characterised in that the reaction is conducted in the presence of ammonium chloride in aqueous medium.

2. A process according to Claim 1 above wherein the reaction is conducted at 125° to 130°C.

3. A process for the manufacture of 6-chloro-7-sulphamyl-3 : 4-dihydro-1 : 2 : 4-benzothiadiazine-1 : 1 - dioxide of the formula shown in Figure 1 of the accompanying drawings substantially as described and ascertained herein or by a process which is an obvious chemical equivalent thereof.

4. 6-chloro-7-sulphamyl-3 : 4-dihydro-1 : 2 : 4 - benzothiadiazine-1 : 1-dioxide whenever prepared by a process of manufacture as claimed in Claims 1 to 3 above.

P. N. BRAHMACHARI,

Partner,

THE BRAHMACHARI RESEARCH INSTITUTE.

Dated this 28th day of December 1960.

Price : TWO RUPEES.

MGIP Santh.—SL—102 Patent/62—22-5-63—100.

THE BRAHMACHARI RESEARCH INST.

NO. 74705 OF 1960

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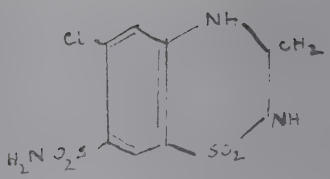

Fig. 1.

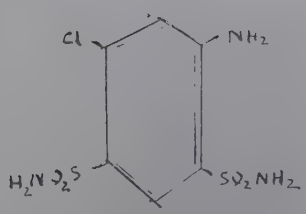

Fig. 2.

For The Brahmachari Research Institute

Partner.

REG. NO. 2273 E 44—106'63.

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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.
Specification No. 74706, dated 28th December 1960, 7 Paus 1882 (Saka). (As accepted 5th June 1962.)

PROCESS AND APPARATUS FOR CONTINUOUS CELLULOSE DIGESTION.

AKTIEBOLAGET KAMYR, OF KARLSTAD, SWEDEN, A COMPANY ORGANIZED AND EXISTING UNDER THE LAWS OF SWEDEN.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to a novel method of continuous cellulose digestion and to a digester apparatus for practicing said method. More particularly, this invention relates to a novel cellulose digestion process including a novel method of heating and supplying the digesting liquor and cellulose fiber material in and to a continuous cellulose digestion process, and novel apparatus for carrying out said method.

Continuous cellulose digesters of several types are well known in the prior art and generally comprise the digester and external circulation conduits connected to the digester. The raw cellulose fiber material (for instance, wood chips and straw) is characteristically charged first into the conduit and carried by the liquor or black liquor circulating therein into the digester. The digester liquor is then separated from the fiber material by drawing it through a sieve attached to the digester and the liquor returned to the circulation conduit. The heat required to maintain the desired temperature in the digester is generally supplied by continuously circulating the digester liquor in a second external circulation conduit, provided with a suitable heat exchanger, and then returning the heater liquor to the digester. For this purpose, the digester chamber has to be provided with internal sieve girdle. Such a method has been described in U.S. Patent No. 2,459,183 issued to one of us.

Charging the fiber material has been accomplished by providing a suitable charging valve in the first circulation conduit. The digester liquor is discharged therein and returned to the digester by means of a high pressure pump. In such cases, any high degree of heating of the digester liquor cannot be performed in connection with that charging and the discharged cooking liquor from the digester would obviously boil violently on account of the high pressure drop connected with its discharge.

In some instances, it is also known to provide a digester apparatus where the fiber material is supplied thereto by circulating black liquor from the digester through the fiber supply means, in some instances with a heat exchanger in the black liquor circulation path. Operating in this manner, the fiber material is introduced at the bottom of the digester and flows upwardly therein countercurrent to the flow of a digesting liquor which is introduced at the top of the digester. In this method of operation, the black liquor is circulated at very high velocity through a narrowed conduit to carry the fiber material (of lighter specific gravity) downward to be introduced at the bottom of the digester. This technique will not, however, supply adequate heat to operate the digester, the temperature therein being maintained primarily by first heating the fresh digesting liquor supply, introduced elsewhere into the digester. Such a method and apparatus is described in U.S. Patent No. 2,359,543.

This invention is designed to overcome the disadvantages present in such prior techniques and apparatus. In particular, the object of this invention is to provide a simplified process of heating and supplying the digester liquor and fiber material to the digester.

An object of this invention is, therefore, to provide in combination with a digester, a digesting liquor circulation path provided with heating means and a charging valve so designed and situated in the circulation conduit that heating of the liquor therein and the steam formed thereby can be collected directly underneath and adjacent the charging valve. In connection with the accomplishment of this objective, a feature of the invention is to provide a charging valve to deliver the cellulose fiber material directly into an enlarged portion of the circulation path. This enlarged portion is such that a fairly spacious steam container chamber is provided. The steam container chamber valve device are located at a higher level than the digester and the flow of steam will be countercurrent to the flow of the supply feed in the charging valve, gravity contributing to the feeding of the fiber material into the circulation path. In this apparatus, the conduit is so designed that it can be maintained filled with steam, the steam thereby being discharged simultaneously with the fiber material being charged.

It will be seen that the invention simplifies the digester apparatus by combining the two circulation conduits previously used, as mentioned above. In addition, since the temperature and the heat required for digestion is supplied to the digester together with the fiber material, digestion starts immediately at the charging end of the digester. As a result of this feature, the volume of the digester can be reduced as compared to known digesters in which the digesting liquor is heated by means of a lye circulation path located at a distance from the charging end, and the sieve girdles and additional circulation lines are eliminated.

The above objects of the invention are accomplished in connection with an upright digester provided with a sieve and screw feeding means at the top thereof and which operates by co-current flow of the digesting pulp and liquor.

A further object of the invention is to provide a novel continuous process for cellulose digestion of comminuted cellulose fiber material, such as wood chips, and straw, where successive portions of such material are introduced into a heated circulating digesting liquor and the fiber material is then conveyed to the digester in co-current flow with the digesting liquor, wherein the temperature of the heated circulating digesting liquor is at least substantially equal to the maximum digesting temperature.

Another object of the invention is to provide such a process of fiber material introduction as just described wherein fiber material is introduced into the heated circulating digesting liquor in the presence of steam, the pressure of the steam being substantially equal to the digesting pressure.

Still a further object of the invention is to provide a process where the cellulose fiber material is first heated by condensing steam thereon, and is then introduced in the presence of steam at a pressure substantially equal to the digesting pressure into heated circulating digesting liquor and conveying co-currently therewith into the digesters, the temperature of the digesting liquor being at least substantially equal to the maximum digesting temperature.

In accomplishing the above described processes of the invention, it will be seen that the heated circulating liquor is obtained by sieving off a substantial portion of the digesting liquor from the fiber material as the latter is introduced into the digester, and then heating the liquor in the circulation path prior to re-mixing it with successive portions of the fiber material.

Accordingly the present invention provides a continuous process for cellulose digestion of comminuted cellulose fiber material which comprises introducing successive portions of said material into a single stream of heated circulating digester liquor and conveying said fiber material to a digester in co-current downward flow with said digester liquor, wherein the temperature of the heated circulating liquor is at least substantially equal to the maximum digesting temperature.

Additional objects of this invention will be apparent from the following description thereof.

Price : TWO RUPEES.

The accompanying drawing schematically illustrates one form of the apparatus which may be used in the practice of this invention.

In the drawing, an upright cylindrical digester 11 is illustrated having a sieve housing 17 attached to the upper end and a pulp discharge line 15 controlled by valve 13 connected to the lower end. Cylindrical sieve 19 is disposed within sieve housing 17 and is provided with a coaxial feeding screw 21 driven by motor 23. Discharge conduit 29 communicates at one end with space 27 between sieve housing 17 and sieve 19 and at the other end with the suction side of circulating pump 31. The pressure side of pump 31 is connected to circulation conduit 25 which is fitted with heater means 33. Circulation conduit 25 empties into a charging valve generally illustrated at 35 through inlet 41. Charging valve 35 comprises a valve housing 36 fitted with inlets 39 and 41 and outlet 43, and rotor 52 having charging passageways 53 is mounted in valve housing 36. Valve outlet 43 empties into steam container chamber 37 which is fitted with a level control 55, schematically shown. The lower end of chamber 37 empties into conduit 26 which penetrates the wall of sieve housing 17 and inside of the sieve 19, as shown. Discharge conduit 29, pump 31, circulation conduit 25, (with heater means 33), charging valve 35, chamber 37, and supply conduit 26, form a loop, for the circulation path for the digesting liquor. It will be noted that the entire loop is above digester 11 and valve 35 and chamber 37 are disposed above sieve housing 17. Feed inlet 39 is supplied with wood chips or straw, etc., from hopper 45 through pipe 46 by supply screw 47, driven by motor 48. Digesting liquor supply conduit 49, fitted with valve 50 and water or black liquor supply conduit 51 fitted with valve 57, are also emptied into feed inlet 39. Partition 56 is arranged in feed inlet 39 to prevent dispersing of the chips and digesting liquor collected in said feed inlet during operation, as will be described hereinafter. Steam conduit 38 supplies steam to the heater device 33 as controlled by valve 34, and through steam line 40, controlled by valve 59, to liquor inlet 41 of housing 36.

In operation, the cellulose starting material, such as wood chips or straw, of suitable particle size are fed to hopper 45 and by means of supply screw 47 into feed inlet 39. Digesting liquor, as needed, is supplied through supply conduit 49. Water or black liquor can also be supplied through supply conduit 51, as will be explained hereinafter. Generally, the quantity of fresh digesting liquor entering through supply conduit 49, will be controlled by valve 50, to correspond to the quantity of chips or straw.

With rotor 52 turned so that passageways 53 are in the vertical position, said passageways will be filled with a supply of chips and digesting liquor from feed inlet 39. After the rotor 52 is turned to the initial shut off position, passageways 53 and the contents thereof will be under atmospheric pressure.

During this short time, it will also be shut off from connection with the circulation conduit 25 which is under digester pressure. Immediately before the charging passageway 53 reaches the position shown in the drawing, its lower end is put into communication with the partly steam-filled container chamber 37. At this point, steam will flow into the passageways 53 and compress its content of chips and air. On further rotation of the rotor 52, passageways 53 reach the position illustrated and the upper end thereof is then open to liquor inlet 41. The heated liquor circulating from conduit 25 then flushes through the passageways 53 and carries the charge therein with it into chamber 37. On further turning of rotor 52, passageways 53 are shut off from liquor inlet 41 and any digesting liquor lye remaining in the passageways flows out through outlet 43 and is replaced by steam from container 37, entering in countercurrent flow. When the passageways are then shut off from valve outlet 43, upon further rotation of the rotor 52, it will contain merely steam of digester pressure. When the passageways are again put into communication with inlet 39, the steam in the passageway will expand and condense on the chips in feed inlet 39 and in supply screw 47 so that the chips are heated. At this stage, partition 56 serves to convey the steam upwards and undesirable displacement of chips and digesting liquor collected in inlet 39 is avoided.

The supply of cellulose fiber material and digesting liquor from charging passageways 53 is thus delivered to the high pressure side of charging valve 35 into chamber 37. From chamber 37, it will flow through supply conduit 26 into the internal portion of sieve 19 near the upper end of feeding screw 21. Feeding screw 21 will move the mixture downward into digester 11, but during this time the main portion of the digester liquor will be sieved off into space 27 and hence only a concentrated mixture of fiber material and digesting liquor will enter digester 11.

Circulating pump 31 serves to such the digesting liquor through sieve 19 and withdraw it from space 27 through discharge conduit 29, connected to the suction side of pump 31. From the pressure side of pump 31, the digesting liquor is fed to heater device 33. Preferably, heater device 33 is designed as a heat exchanger for indirect heating of the digesting liquor flowing therethrough, and may be heated by means of steam supplied through steam conduit 38. Alternatively, heater device 33 may be arranged for direct heating by steam; however, the digesting liquor will then be diluted with steam condensate which is often undesirable.

Substantially, the entire heat quantity required for the operation of the digester 11 is supplied to the digesting liquor circulating in circulation conduit 25 through heater device 33 and, as a result, in this invention, sieves in the digester wall or circulation conduits for heating the liquor below sieve housing 17 are eliminated. By way of example, in common sulfate digestion, the temperature in the digester is generally desired to be at a level of about 170°C. and, accordingly, in operation of the invention, the circulation liquor in heater device 33 is raised to a temperature of approximately 176°C. In chamber 37 where the heated liquor is intimately mixed with the introduced feed of chips and fresh digesting liquor and during the supply feeding operation to sieve 19, this temperature will gradually drop to about 171°C., this being the temperature of the circulating liquor en return to the heat exchanger 33 after egress through the discharge conduit 29.

Thus, in a plant for production of 150 tons of air-dry pulp per 24 hours dry wood chips are supplied to hopper 45, at a rate of about 200 kilograms per minute. With normal moisture content said quantity of wood chips contains about 100 to 200 liters of water. A liquor quantity of about 200 liters heated to about 75°C. is simultaneously supplied through digesting liquor supply conduit 49. The quantity of water or black liquor entering through supply line 51 may be up to 50 liters per minute, as will be explained hereinafter. In order to heat this mixture to the desired 170°C. prior to its delivery into sieve housing 17, with a temperature drop in the circulating liquor in line 25 of only the order of about 5°C., the lye liquor must be circulated at a rate of about 6,000 to 10,000 liters per minute. Feeding screw 21 forcing the chips downwardly past sieve 19 into digester 11 will keep the sieve clean so that this heavy circulation will not become obstructed.

Since the liquor circulation path forms a loop above the level of the top of the digester, and charging valve 35 is disposed at the uppermost part of the loop, the steam formed by the heated liquor in chamber 37 will collect under and close to the charging valve. That is, the steam formed in the chamber 37 above the liquid level maintained by level control 55 will pass upwardly into passageways 53. Consequently, when the rotor 52 is turned so that these passageways are again in communication with feed inlet 39 a quantity of steam will be discharged thereinto equal to the quantity of chips and liquor charged.

This condition is maintained by keeping the liquid level of the container 37 at a point such that it will be partly filled with steam. Level control device 55 accomplishes this by controlling valve 57 in water or black liquor supply line 51. Should the liquor level in chamber 37 drop, as for instance due to an occasional increased discharge through pulp discharge lyine 15, an increased quantity of water or black liquor will be

supplied to conduit 51 so that the desired level will be re-established in the chamber 37. It will be appreciated that the pressure of the digester corresponds to the vapor pressure above the liquor in container 37 which will in this example correspond to the vapor pressure at a temperature of about 173°C.

When the plant is first started, the steam content of chamber 37 can be supplied through steam line 40 controlled by valve 59. The rotor 52 is placed in a position so that passageways 53 are in communication with liquor inlet 41 to permit the steam to enter chamber 37. The steam pressure in steam conduit 38 will be maintained higher than the pressure in digester 11 and, accordingly, steam let by valve 59 will effect the discharge of the feed in passageways 53. Thus, at this stage of operation, the circulating liquor need not be used for that purpose. Instead, the liquor may be led directly into container 37 by means of a bypass conduit (not shown) from circulation conduit 25.

It will be appreciated that the above example of this invention is merely for illustrative purposes thereof. The invention is not limited to particular temperatures and pressure to be employed in the digester or circulation conduits. Generally speaking, the apparatus and method of this invention may be carried out under conditions of temperature and pressure as conventionally used in the art of cellulose digestion and no special requirements therefor are imposed on the process by my novel process and apparatus. Of course, the pressure in the digester will be determined by the temperature employed, as indicated above. The temprature to which the circulating liquor is heated in heater device 33 may also be varied as desired within the skill of the art. Obviously, higher temperatures than the 176°C., mentioned above, may be used if desired, particularly where a digester temperature above 170°C. is contemplated. Furthermore, where the insulation of circulation conduit 25 in steam container chamber 37 and inlet conduit 26 are less adequate than in the particular device to which the above example relates, the temperature drop between the liquir exiting from heater device 33 and that entering heater device 33 are greater and, accordingly, a greater differential will have to be maintained, as will be appreciated. It is also apparent that different supply lines for the starting materials can be used equally well, the figures mentioned above being desirable for optimum production and convenience of operation. Obviously, the rate of discharge of digested pulp through discharge line 15 will be determined by adjustment of valve 13 and will be maintained at a value such that the time of passage of the material through the digester corresponds to the time required for complete digestion of the fiber material. The precise optimum rate will vary according to the particular cellulose fiber material being treated. The rate of introduction of the latter through feed inlet 39 will be determined by the said rate of discharge through discharge line 15.

Equally well, the above-described specific embodiment of the apparatus may also be modified in other respects. For instance, a charging valve device of some other design may be used, or said device may be replaced by a piston or screw feeding device. In addition, if desired, the sieve housing 17 at the upper end of the digester may be modified by placing the sieve 19 and coaxial feeding screw in a horizontal or inclined position.

Accordingly, it will be understood that this invention is not limited to the specific embodiments hereinabove described and illustrated but only by the spirit and scope thereof as defined by the following claims.

We claim:

1. A continuous process for cellulose digestion of comminuted cellulose fiber material which comprises introducing successive portions of said material into a single stream of heated circulating digester liquor and conveying said fiber material to a digester in co-current downward flow with said digester liquor, wherein the temperature of the heated circulating liquor is at least substantially equal to the maximum digesting temperature.

2. The continuous process for cellulose digestion of Claim 1, which comprises, circulating digester liquor withdrawn from a cellulose digester through a liquor-circulating loop, introducing successive portions of said fiber material into said circulating digester liquor at a point in said loop filled with steam and located higher than the point where said liquor is withdrawn from said digester, while heating said circulating digester liquor intermediate the point of its withdrawal from the digester and the point of introduction of said fiber material.

3. A continuous cellulose digester apparatus for carrying out the process as claimed in Claim 1 comprising an upright digester, sieve means at the upper end of said digester, a feeding screw disposed coaxially in said sieve means, an outlet circulation conduit externally communicating with said sieve means, means for heating the liquor circulating in said outlet circulation conduit, an inlet conduit communicating internally with said sieve means, and charging valve means, said charging valve means including a housing arranged intermediate said outlet circulation conduit and said inlet conduit and communicating therewith, and a feed inlet communicating with said housing, for introducing cellulose fiber material into said inlet conduit.

4. The continuous cellulose digester apparatus of Claim 3, wherein said charging valve means is disposed above said inlet conduit and the portion of said inlet conduit in communication with said housing is of substantially greater diameter than the remaining portion of said inlet conduit, so as to provide a steam container chamber immediately below said charging valve means.

5. The contiuous cellulose digester apparatus of Claim 4, wherein said steam container chamber is higher than the remaining portions of said inlet conduit.

6. The continuous cellulose digester apparatus of Claim 4, wherein said steam container chamber is provided with level control means for maintaining said steam container chamber partly filled with liquid and partly filled with steam.

7. The continuous cellulose digester apparatus of Claim 3, wherein said charging valve means include means for alternative communication with said feed inlet for introducing cellulose fiber material into said charging valve means, and communication with said outlet circulation conduit and said inlet conduit, for circulating heated digester liquor through said charging valve means and introducing said fiber material into said inlet conduit.

8. The continuous cellulose digester apparatus of Claim 7 in which the inlet valve means includes a rotor having an internal passageway communicating with spaced points on the rotor, the outlet conduit and inlet conduit being spaced to communicate with the passageway simultaneously as the rotor is turned whereby heated digester liquor will pass through said passageway when the valve is in communication with the outlet conduit and the inlet conduit.

9. The continuous cellulose digester apparatus of Claim 7, wherein said feed inlet is provided with conduit means for introducing fresh digesting liquor and conduit means for introducing a supply of black liquor.

10. Continuous cellulose digester apparatus claimed in Claims 3 to 9 comprising an upright digester and sieve means arranged at the top thereof, a coaxial feeding screw arranged internally of said sieve means, an outlet circulating conduit communicating externally with said sieve means and an inlet conduit communicating internally with said sieve means, pumping means and heater means arranged in said circulation conduit and charging valve means arranged intermediate and in communication with said circulation conduit and said inlet conduit, a steam container chamber comprising a widened portion of said inlet conduit, arranged below said charging valve means and above the remaining portion of said inlet conduit, a feed inlet communicating with said charging valve means for introducing cellulose

fiber material and digester liquor supply means and black liquor supply means for respectively introducing said digesting liquor and said black liquor into said feed inlet, and level control means operatively connected between said steam container chamber and said black liquor supply means for maintaining said steam container chamber partly filled with liquid and partly filled with steam.

11. A continuous process for cellulose digestion of comminuted cellulose fiber material substantially as hereinbefore described with reference to and as shown in the accompanying drawings.

R. HALL

OF REMFRY & SON,

Agent for the Applicants.

Dated this 28th day of December 1960.

M.G.P. Smith.—S.L.—105 Patent, 62—18-4-63—100.

AKTIEBOLAGET KAMYR.
No. 74706 of 1960.

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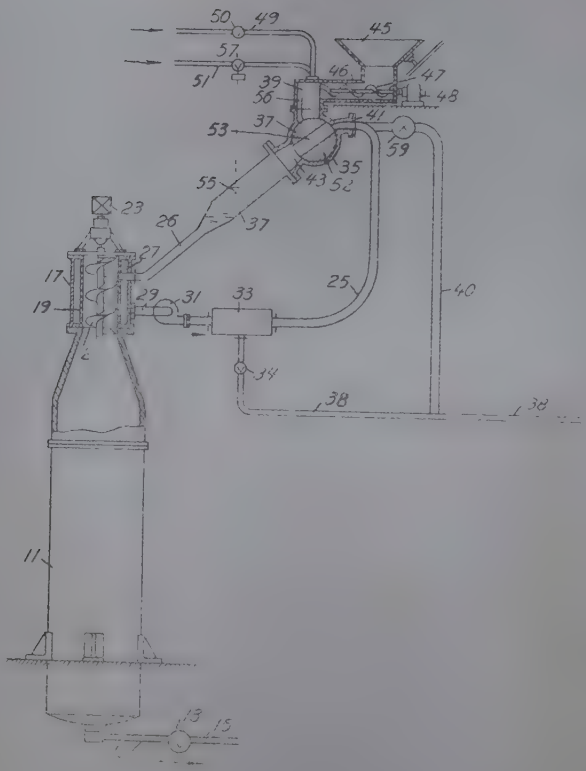

Hall

of KEMPE & SOV
Agent for the Applicants

[illegible] INSTITUTE [illegible]

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74707, 28th December 1960/7 Paus 1882 (Saka.) (Accepted 26th April 1962.)

DEVICE FOR DISCHARGING MATERIALS FROM PRESSURE VESSELS.

AKTIEBOLAGET KAMYR, OF KARLSTAD, SWEDEN, A SWEDISH COMPANY.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to devices for discharging fibrous or like material from a pressure vessel. It has particular application to the discharges of finely comminuted fibrous material such as wood chips, cut wood, bamboo, concentrated suspensions of digested cellulose pulp and the like from an upright or substantially upright pressure vessel, such as a reaction tower, a steaming vessel, a prehydrolysis treatment vessel, a digester for chemical or semichemical pulp, a bleaching tank and the like.

Due to the high pressures prevailing in such vessels as those referred to, the fibrous material has a tendency to compact itself at the outlet and clog the same. The problems presented thereby are aggravated by a pressure drop usually taking place in the outlet proper. Another problem resides in that the material tends to flow faster through the vessel at certain regions, usually the transverse center regions, whereas along the walls of the vessel the material moves more slowly in the passage through the vessel.

The principal object of the invention is to eliminate these and other problems by providing a pressure vessel, of the type referred to, with a novel means for facilitating satisfactory and desirable discharge of the material therefrom.

Further objects reside in the provision of novel structures, and arrangements thereof in connection with pressure vessels, of the type referred to, for effecting a steady and uniform flow of material to the outlet of the vessel and for conveying the material away from said outlet.

According to my invention, it is contemplated that an outlet be formed at or near the bottom of the pressure vessel and that above the outlet there is arranged an essentially horizontal bottom plate means rotatable about a vertical axis, said plate means being shaped as a helical surface in order to be operable, during rotation, to gradually transfer to the space below the bottom plate means the lowermost layer of the fibrous material column resting upon the upper face of the bottom plate means, so that the column drops uniformly over the entire transverse sectional area of the vessel. It is further contemplated that the material column be supported by the rotatable plate means, that the weight of the column of material in the vessel will not in any way effect the conditions at the outlet proper, and that the material gradually separated from the column by the plate means pass through the outlet in a loose form or as a fluent suspension.

Further objects and advantages of the invention will be in part obvious and in part pointed out hereinafter.

The novel features of the invention may be best made clear from the following description and accompanying drawings in which:

Figure 1 is a fragmentary vertical sectional view of a pressure vessel equipped with one embodiment of my invention;

Figures 2 and 3 are horizontal sectional views taken respectively on lines II-II and III-III of Figure 1;

Figure 4 is a view corresponding to Figure 1 and showing another embodiment of my invention;

Figures 5 and 6 are horizontal sectional views taken respectively along lines V-V and VI-VI of Figure 4.

Referring to the illustrative embodiment shown in Figure 1, 11 designates the lower end of a standing cylindrical pressure vessel, the upper end of which (not shown) is continuously charged in any suitable manner with chips, for example, which chips may be moistened with any suitable treating liquid or merely with water, as is known. The vessel 11 is closed and through a conduit (not shown) steam is supplied, whereby the chips are heated to a temperature which, depending upon the treatment involved, may lie somewhere between 110 and 200 degrees centigrade. Due to this steam filling operation, the vessel is maintained under a corresponding overpressure, i.e., a pressure above atmospheric, and for example, of the order of 8 atmospheres gauge.

At its lower end the cylindrical part of the vessel 11 merges into a downwardly and inwardly tapering, funnel-shaped portion 13 terminating in an eccentrically located outlet 15. Disposed at the outlet 15 may be a horizontal screw conveyor 17 and a conventional defibrator or defibering device 19, both of which may be driven by suitable connection to a motor 21.

Mounted in vessel 11, preferably substantially at the level where the cylindrical portion and the inverted generally conical portion of the vessel join, is a rotatable horizontal bottom plate means. This means supports the column of material in the vessel so that the funnel-shaped portion is relieved of the weight of the column of material. As best seen in Figures 1 and 2 two helical flights 23, 25 define the plate means. As shown, these flights are attached to a centrally disposed and upright conical member 27. Member 27 is shown fixedly mounted on the upper end of a centrally located vertical driving shaft 29, journalled in portion 13 and extending through a stuffing box 31 or the like carried by the wall of the portion 13.

A motor 33 and conventional speed reducing gear arrangement 35 may be operatively connected to shaft 29, as shown, to rotate the latter at a relatively low speed, for instance 1/4 to 2 revolutions per minute, and in the direction indicated by arrows in Figure 2. 37 designates radially extending braces for the shaft 29, suitably arranged within the vessel, for example, adjacent to and below the member 27, as shown.

The helical flights 23 and 25 preferably are of the relatively flat configuration shown, extending throughout an angle of approximately 180°. These flights, as indicated, preferably are arranged substantially at the same elevation with the radial leading edge 43 of flight 25 being substantially at the same level on member 27 as the radial leading edge 49 of flight 23 and approximately 180° outlet of phase therewith, as best seen in Figure 2. The radial trailing edges 45, 47 of flights 23, 25 respectively likewise preferably are disposed at substantially the same level on member 27 and approximately 180° out of phase with each other.

The leading edges of the flights are spaced above the trailing edges to define radially extending passageways 39, 41 therebetween, as shown in Figure 2. In this embodiment, the leading edges 43, 49 are also slightly spaced laterally from the adjacent trailing edges 45, 47 respectively whereby the radial passages 39, 41 also define narrow vertically extending openings or passages.

As shown, the flights 23, 25 extend radially outwardly from member 27 to the immediate vicinity of the adjacent cylindrical wall of the vessel 11 to prevent the material from discharging through the space between the flights and the adjacent vessel wall. Hence, the only passage for the material will be the openings 39, 41.

The vertical gaps or spaces formed between the edges 43 and 45, and also between the edges 47, 49, as is evident, will be of a height corresponding to the pitch of one-half of the circumference of the helical surface of the two flights 23, 25. If the diameter of the vessel 11 and the combined flights 23, 25 is of the order of 2,000 to 3,000 mm, the height of these gaps may be approximately 150 to 300 mm.

When the shaft 29 is rotated to rotate the flights in the direction of the arrows in Figure 2, the leading edges 43, 49 will function similarly to the cutting edges of an auger or similar tool, and will separate off a layer of material from the lower end of the material column, such layer having a thickness corresponding to the height of the aforesaid gaps between the upper leading edges 43, 49 and the lower trailing edges 45, 47. The chips of such layer will be transferred through the openings 39, 41 to the space below the flights, as will be understood.

The height of the aforesaid gap enables comparatively coarse chips as well as knots and splinters therein to pass through such openings 39, 41 without tending to clog or form plugs. By virtue of the adhesive and/or cohesive forces between the chips, bridges are formed over the openings 39, 41 when the flights are stationary so that chips are fed therethrough only when the flights are rotated. When the material is more finely comminuted, the flights may be designed to extend over an angle greater than 180°, so that they partially overlap each other; in other words, so that the leading edges 43, 49 would overlap the adjacent trailing edges 45, 47 respectively. Then the passages between the adjacent leading and trailing edges will be directed parallel to the helical surfaces of the blades, i.e., essentially horizontal.

Attached to the inside of the vessel wall immediately above the bottom plate is a plurality of radially arranged fins 51 for the purpose of preventing the column of chips from rotating together with the flights 23, 25. Thus when the flights are rotated, the column of chips will move only in vertically downward direction, and continuously and uniformly. Only adjacent the member 27 may a slight lateral displacement take place, otherwise there is no rearrangement or internal movement in the column of chips which could give rise to disturbances of or irregularities in the even and uniform descent of the chips column.

After the chips have passed through the flights 23, 25, they drop through the steam-filled funnel 13, which is practically empty of chips. In order to prevent chips from jamming between the wall of the funnel 13 and the shaft 29, an upwardly tapering fin 53 may be arranged in the space therebetween, as shown. At the outlet 15 the chips enter the thread of the screw conveyor 17 and are carried by the same to the device 19, from which the chips are delivered through the conduit 55 and at a reduced pressure. The screw of the conveyor 17 preferably is driven at such a high speed that chips will not collect in the outlet 15, therefore eliminating the possibility of having the outlet clogged by pluge or bridges of chips.

The embodiment shown in Figures 4—6 differs from that of Figures 1—3 essentially only with respect to the manner of discharging the chips from the funnel-shaped space below the rotating flights. Similar reference characters have been used to designate similar parts in the two embodiments. The discharge in the Figure 4 embodiment is assigned by means of a circulating liquid supplied through a number of nozzles 57 arranged below the flights 23', 25' in the portion 13', and preferably being tangentially directed to circulate liquid in a direction opposite to the direction of rotation of the flights.

The chips dropping through the flights are whirled up in the liquid introduced through nozzles 57 and form a suspension which readily flows through the outlet 15' of the funnel portion 13'. A conduit 61 is connected at one end to a valve 62 connected to the outlet 15'. The other end of conduit 61 is connected to a screw conveyor 63, the shaft of which is inclined upwardly, as shown. The screw of the conveyor preferably is enclosed by an inner, perforated or sieve-like housing 65, said housing being in turn enclosed by an outer housing 67.

The liquid drained from the chips through housing 65 collects in the space between housings 65 and 67, and is returned by a pump 69 through the conduit 71 to the flushing nozzles 57. An annular pipe 72 may be provided to connect conduit 71 with the nozzles 57, the pipe 72 encircling vessel 11', as indicated.

A conduit 74 leads from the upper discharge end of conveyor 63 to a valve 73 through which the chips are transferred to a higher or lower pressure for further treatment, or the chips may be transferred to atmospheric pressure. Valve 73 is of the type designed to permit material to flow therethrough without letting the pressure in conduit 74 be influenced or changed by the pressure at the downstream or outlet side of the valve. Hence, the pressure in the vessel 11' will be maintained. Said valve 73 is preferably of the rotary type including a plurality of rotating pockets or cells defined by radial walls.

Since some liquid may be discharged through conduit 74 with the chips, a line 75 may be provided opening into housing 67, as shown, and communicating with a source of liquid (not shown) to permit introduction of additional liquid into the housing, as desired.

Thus, it will be possible to insure that a sufficient quantity of liquid for flushing through nozzles 57 will be provided in the housing 67. The quantity of circulating liquid will depend on the size of the chips and the shape of the bottom of the vessel. As an example, this quantity may be between 10 and 80 liters per kilogram of the chips flushed out of the vessel 11'.

This procedure of discharging the material from the vessel by utilizing circulating liquid may also be used in the situation where the chips in the vessel are mixed with a treating liquid and the column of chips is completely or partially submerged below the level of such treating liquid. If the vessel is completely filled with treating liquid, the chips must be sufficiently impregnated by the liquid so that they do not float but rest upon the rotating helical flights with at least part of their weight.

As is evident, discharging devices according to the invention may also be used in pressure vessels in which cellulosic pulp of a high consistency, for instance a dry content of 15 per cent. or higher, has been subjected to some treatment, for example, bleaching. It will further be evident that still other materials may be satisfactorily discharged in accordance with the teachings of this invention.

If desired, the plate means at the bottom of the vessel may be composed of three, four or more helical flights in lieu of the two shown, or it may be designed as a single screw thread extending through approximately 360°. The stationary bottom of the vessel may be formed as an annular groove and an impeller or similar means may be arranged therein in order to cause a heavy flow of circulating liquid, whereby the fibrous material is held in suspension so that it is easily flushed out through the outlet.

The present invention will thus be seen to completely and effectively accomplish the objects enumerated hereinabove. It will be realized, however, that various changes and substitutions may be made to the specific embodiments disclosed herein for the purposes of illustrating the principles of this invention, without departing from these principles. Therefore, this invention includes all modifications encompassed within the spirit and scope of the claims.

We claim:

1. In a device for discharging materials from pressure vessels, an upstanding vessel for containing a column of fibrous material or the like, an outlet at the bottom of said vessel, means for feeding such material to said outlet, said means including a substantially horizontally disposed plate means arranged above said outlet for rotation about a vertical axis, said plate means being defined by a helical surface on which the material is adapted rest and which is operable during rotation thereof to gradually transfer material from the column toward said outlet.

2. The structure defined in Claim 1 wherein said plate means includes two helical flights arranged at substantially the same level, said flights extending throughout substantially the entire transverse sectional area defined by the adjacent portion of said vessel with through radial passages being formed between said flights for the flow of material therethrough.

3. The structure defined in Claim 2 wherein said helical flights each extend through approximately 180°, the corresponding leading and trailing edges of the flights being spaced approximately 180° out of phase relative to each other, and the radial passages being defined by a lateral spacing between the leading and trailing edges of said flights.

4. The structure defined in Claim 3 wherein a centrally located vertical shaft is journalled in said vessel below said flights, an upstanding conically-shaped member being fixed to the top of said shaft, and said flights being mounted on said member.

5. The structure defined in Claim 4 wherein that portion of the vessel below said flights tapers downwardly and inwardly terminating in said outlet, and said outlet being eccentrically disposed relative to said shaft.

6. The structure defined in Claim 5 wherein conveyor means are provided in operative connection with said outlet for conveying the material therefrom.

7. The structure defined in Claim 6 wherein said conveyor means is a screw conveyor having an inclined axis of rotation, and a perforated housing enclosing said screw conveyor for the passage of liquid radially from the material being axially conveyed through the housing.

8. The structure defined in Claim 7 wherein nozzle means are provided opening tangentially into the downwardly and inwardly tapering portion of said vessel, and means communicating with said nozzle means and said perforated housing for delivering to said nozzle means the liquid passing through said perforated housing.

9. The structure defined in Claim 8 wherein said nozzle means are disposed to induce an angular flow of liquid below said flights and circulating in a direction opposite to the direction of rotation of said flights.

10. The structure defined in Claim 1 wherein nozzle means are provided below said plate means and opening in a tangential direction into said vessel, and means for supplying fluid to said nozzles.

11. A device for discharging fibrous or like material from a pressure vessel substantially as hereinbefore described with reference to and as shown in the accompanying drawings.

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or REMFRY & SON.
Agent for the Applicants.

Dated this 28th day of December 1960.

M(1)PC—No—87 Patent/63—2·3·63—100.

Fig. 1

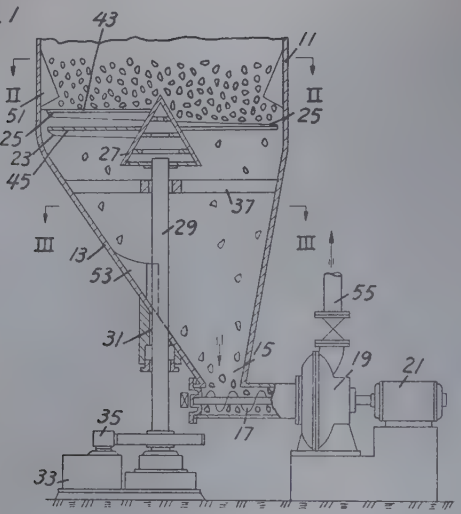

Fig. 2

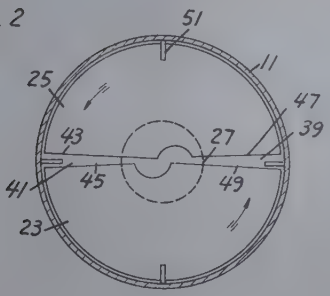

Fig. 3

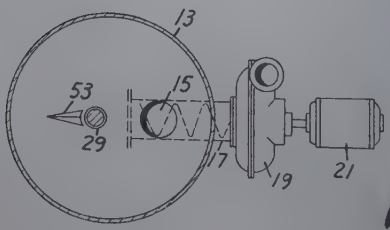

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Fig. 4

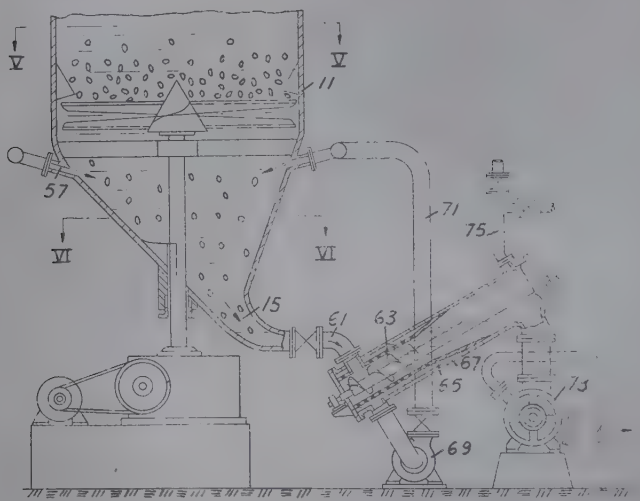


Fig. 5

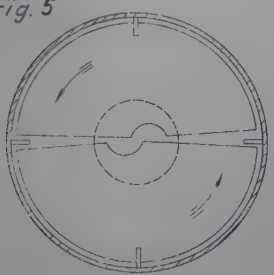
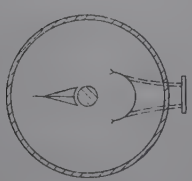


Fig. 6



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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.
Specification No. 74708, 28th December 1960. 7 Paus 1882 (Saka). Accepted 20th June 1962.

METHOD AND APPARATUS FOR THE LIBERATION OF CELLULOSIC FIBER MATERIAL.

AKTIEBOLAGET KAMYR, OF KARLSTAD, SWEDEN, A SWEDISH COMPANY.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

The present invention relates to a method and apparatus for the liberation of cellulosic fibre material by its digestion with a digesting liquor at elevated pressures and temperatures in a continuous cellulose digester.

It is known to discharge the pulp consisting of digesting liquor and liberated fiber material through the outlet of the digester at a substantially constant temperature into a blow tank under a considerably reduced pressure, in which blow tank digesting liquor loses much of its heat content through the liberation of steam therefrom, such steam being used for various heating purposes, such as preheating the fiber material to be charged into the digester, as is understood. This preheating, for example, takes place in a steaming vessel connected to the digester inlet.

It has been proposed to lower the temperature at the outlet end of the digester in order to enable the pulp to withstand mechanical stresses accompanying discharge without having its quality impaired. However, such temperature reduction is usually effected by pumping a relatively cool fluid into the digester at its outlet, thereby reducing the temperature of the digesting liquor and pulp. As a consequence, when the pulp reaches the blow tank, there will be considerably less steam liberated from the pulp in the blow tank, and hence, less heat available for preheating.

The main objective of the present invention, therefore, is to provide an improved method and apparatus of the character described permitting use of the heat content of the pulp for producing an ample quantity of low pressure steam and at the same time effecting a desired cooling of the pulp before its discharge from the digester.

According to the invention, this objective is attained by providing a method for the liberation of cellulose fiber material by digestion thereof with a digesting liquor at an elevated pressure and an elevated temperature in a continuous digester having an inlet and an outlet; said method comprising the steps of withdrawing digesting liquor from said fiber material and said digester substantially immediately before said material leaves said digester; reducing the pressure and temperature of said withdrawning digesting liquor externally of said digester by the liberation of steam from said withdrawn digesting liquor; returning to said digester adjacent the outlet thereof at least some of the remainder of the withdrawn digesting liquor at its reduced temperature; and introducing steam liberated from the withdrawn digesting liquor into a steam vessel connected to the inlet of said digester.

It is contemplated that apparatus embodying the invention include, in a continuous digestion system, means defining a circulation loop for withdrawing digesting liquor from adjacent to and up-stream of the digestor outlet, with a steam separating means being provided in said circulation loop and having a digesting liquor inlet, a digesting liquor outlet, and a steam outlet.

Other objects will become apparent as the description proceeds.

The invention may best be made clear from the following description considered together with the accompanying drawing wherein a continuous digestion apparatus embodying the invention is shown diagrammatically.

In the drawing, the numeral 11 designates a steaming vessel for heating a mixture of a suitable digesting liquor and wood chips or other comminuted cellulosic fiber material ,supplied to a hopper 13 and charged or fed into the steaming vessel 11 by a low-pressure charging apparatus 15. Low-pressure steam for such heating is supplied through a conduit 17, while the material is stirred and conveyed toward the outlet end of the steaming vessel by means of a conveyor screw 19. A desired superatmospheric pressure in the steaming vessel preferably about 1 atmosphere gauge, is maintained by means of an automatically controlled vent valve 21.

The hopper 13, feeding device 15, steaming vessel 11, conveyor 19 and valve 21 are all of conventional construction, as will be understood.

From the steaming vessel, the fiber material is transferred by means of a known high-pressure charging apparatus 24 to the upper end of a standing cylindrical digester 25 of suitable construction. In this digester, the material is heated, *e.g.*, to about 170°C., by means of high-pressure steam supplied through conduit 26. Additional heating may be provided by the circulation of digesting liquor in an outer loop connected to the upper part of tht digester and passing through a heat exchanger (as shown, *e.g.*, in U.S. Patent No. 2414062). A pressure of the order of 10 atmospheres gauge is maintained in the digester.

During the slow and even downward movement of the fiber material through the digester, a reaction with the digesting liquor takes place so that the fiber material is completely digested when it reaches the outlet 27 of the digtster, at the lower end thereof. The pulp is shown as being fed down into outlet 27 by means of a motor-driven rotary scraper 29 and is transferred through a conduit 31 having a valve 32 therein to a blow tank (not shown) or similar device, where a reduced superatmospheric pressure is maintained, and the pulp then goes to washing, etc., as is understood.

According to the invention, immediately before the fiber material reaches the digester outlet 27, a part of digesting liquor contained therein is withdrawn. As shown, a sieve-like section 33 is provided for this purpose, being formed in the wall of the lowermost cylindrical part of the digester. This section 33 may extend in a generally horizontal plane through approximately 180° around the circumference of the digester 25 and communicates through a conduit 35 with a steam separator, preferably in the form of a cyclone 37.

Sieve-like section 33 may be of the general type referred to in U.S. Patent No. 2695232, and may be covered by an external blister (not shown) on the digester 25, coextensive with section 33 and providing a space communicating with the lower end of conduit 35, as suggested in the latter patent.

The conduit 35 opens tnagentially through the outer wall of cyclone 37, as should be sevident. A steam outlet 39 is provided in the upper part of the cyclone 37 and opening into conduit 17, with a cylindrical inner wall 41 enclosing said outlet in cyclone 37, as indicated. A liquor outlet 43 is provided at the lower end of the cyclone, as shown.

Thus the outlet 39 communicates through conduit 17 with the steaming vessel 11 wherein the pressure is considerably lower than in the digester. Valve 18 arranged in conduit 17, as indicated, will be opened during operation of the apparatus. Therefore, when the liquor withdrawn from the digester enters the cyclone 37, the liquor is relieved of the greater part of its superatmospheric pressure and gives off a great quantity of steam of the pressure prevailing in the steaming vessel 11. At the same time, the temperature of this liquor is reduced to a value corresponding to the pressure in the vessel 11, *e.g.*, to approximately 120°C. Digesting liquor at this lowered temperature discharges through the outlet 43 of the cyclone.

A conduit 44 is connected to outlet 43 at one end and to a nozzle 47 at the other end thereof, the nozzle 47 being shown as positioned opposite the sieve 33. A high-pressure pump 45 is provided in conduit 44, as shown, for pumping the liquor at the reduced temperature back into the digester adjacent outlet 27 at the proper pressure.

The quantity of liquor circulating in the above-described loop including conduits 35, 44 and cyclone 37 may,

vary, depending upon the steam requirements, between one-third and two-thirds of the liquor content of the pulp quantity passing the digester during the same time period.

From the steam conduit 17, a conduit 20 having a valve 22 therein is shown branching off to a heat exchanger 49, in which steam leaving the cyclone can be used wholly or partly for other heating purposes, *e.g.*, heating of the digesting liquor supplied to the digester, water heating, etc.

A conduit 51 having a valve 52 therein is shown connected to return conduit 44 and through which a liquid, for example, a cooling liquid can be supplied to the liquor in conduit 44 when required, which liquid may be cooled in a cooling device 53, for example, of the closed fluid heat exchanger type, as indicated.

Due to the cooling action effected by the liquor returned through conduit 44, the temperature of the discharged pulp in the digester outlet 27 and the conduit 31 is lowered to approximately 115 to 150°C, in which temperature range the pulp can withstand the mechanical stresses accompanying the discharge of the pulp to atmospheric pressure or a low superatmospheric pressure, without the quality of the pulp being impaired. And, at the same time, sufficient steam is available at appropriate pressures for preheating in vessel 11 by reason of the provision of cyclone 37 and conduit 17, as described heretofore.

The above-described apparatus is merely an example of a practical application of the invention and, as will be appreciated, the details thereof may be modified in various respects. For instance, the sieve section 33 can be arranged as a sieve girdle extending all around the periphery of the digester, as disclosed in U.S. Patent No. 2695232. Furthermore, the sieve may be located in the bottom of the digester below the rotary scraper 29, and the return nozzle 47 may be centrally located, *e.g.*, it may be arranged on or above the upper end of the centrally bored rotary shaft of the scraper 29.

The present invention will thus be seen to completely and effectively accomplish the objects enumerated hereinabove. It will be realized, however, that various changes and substitutions may be made to the specific embodiments disclosed herein for the purpose of illustrating the principles of this invention, without departing from these principles. Therefore, the invention includes all modifications encompassed within the spirit and scope of the following claims.

We claim:

1. A method for the liberation of cellulose fiber material by digestion thereof with a digesting liquor at an elevated pressure and an elevated temperature in a continuous digester having an inlet and an outlet; said method comprising the steps of: withdrawing digesting liquor from said fiber material and said digester substantially immediately before said material leaves said digester; reducing the pressure and temperature of said withdrawing digsting liquor externally of said digester by the liberation of steam from said withdrawn digesting liquo returning to said digester adjacent the outlet thereof a least some of the remainder of the withdrawn digestin liquor at its reduced temperature; and introducing steam liberated from the withdrawn digesting liquor into a steam vessel connected to the inlet of said digester.

2. In a continuous digestion apparatus of the character described and including a digester having an inlet adjacent the upper end thereof and an outlet adjacent the lower end thereof, the improvement which comprises: means defining a fluid circulation loop for withdrawing digesting liquor from adjacent to and upstream of said outlet; steam separating means in said circulation loop and having a digesting liquor inlet, a digesting liquor outlet, and a steam outlet; a steam vessel connected to the inlet end of said digester; means connecting said steam outlet of said steam separating means to said steaming vessel; and means including a high pressure pump for connecting the digesting liquor outlet of said steam separating means to said digester adjacent to and upstream of said digester outlet.

3. A method for the liberation of cellulose fiber material by digestion thereof with a digesting liquor at an elevated pressure and an elevated temperature in a continuous digester having an inlet and an outlet, substantially as hertinbefore describtd with reference to the accompanying drawings.

R. HALL,

or REMFRY & SON,

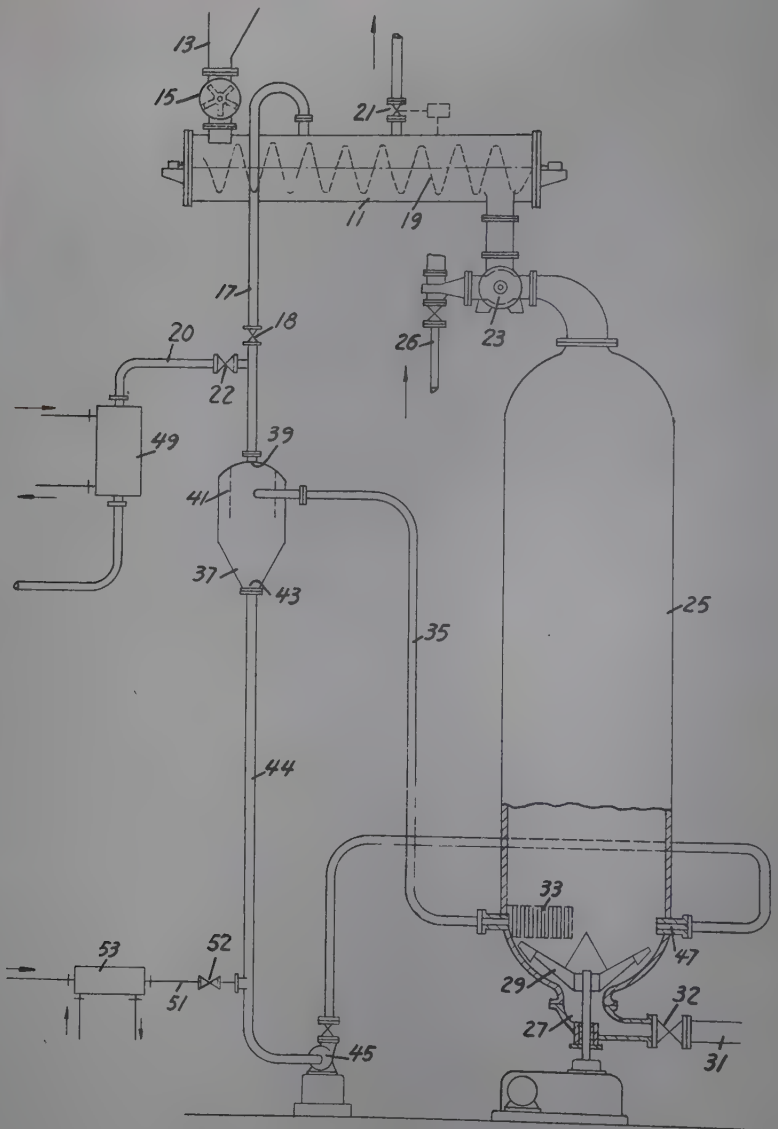
Agent for the Applicants.

Dated this 28th day of December 1960.

MGIP Samth—SL—106 Patent/62—15-7-63—100.

AKTIEBOLAGET KANYR.
NO. 74708 of 1960.

1 Sheet.



of REMFRY & SON
Agent for the Applicants

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Specification No 74709, filed 28th December 1960/7 Paus 1882 (Saka). (Accepted 3rd May 1962.)

METHOD AND PLANT FOR CONTINUOUS CELLULOSE DIGESTION.

AKTIEBOLAGET KAMYR, of Karlstad, Sweden, a Swedish Company.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

The present invention relates to a method and a plant or apparatus for the liberation of cellulosic fiber material by its digestion with digesting liquor at a raised pressure and a raised temperature in a continuous digester.

In apparatus and processes of this type, it is known that the mechanical stresses upon the fiber material, which take place in connection with the mechanical discharge of the fiber material out of the digester and its transfer to a lower pressure, are detrimental to the quality of the pulp obtained, if the fiber material simultaneously is subjected to an attack of unspent digesting liquor of the full digesting temperature.

The object of the invention is to improve the pulp quality, in methods and plants, as referred to, by decreasing the possibility of a chemical attack during the discharge of the pulp from the digester; and the essential characterising feature of the invention resides in that a part of the digesting liquor is withdrawn from the fiber material immediately before the same passes out through the digester oulet and in that this withdrawn digesting liquor is replaced by a weaker liquid which then accompanies the fiber material out through the digester outlet. Preferably, this weaker liquid consists of digesting liquor diluted by wash-water and taken from a device for washing the digested fiber material, e.g., a wash filter, disposed downstream from the digester.

The invention accordingly provides a method of liberating cellulosic fiber material by digestion thereof with a digesting liquor at a raised pressure and a raised temperature in a continuous digester having an inlet and an outlet, said method being characterised in that a part of the digesting liquor is withdrawn from the fiber material immediately before the same passes out through the outlet of the digester, and in that said withdrawn digesting liquor is replaced by a weaker liquid at least a portion of which has previously passed through the digester outlet together with the fiber material.

Usually, in practicing this invention, the replacement liquid is of a temperature considerably lower than the digesting temperature and accordingly, in the digester outlet, the fiber material will desirably be mixed with a liquid which in comparison to the aforesaid withdrawn digesting liquor is weaker as to its content of chemicals as well as being cooler and, therefore, less detrimental than the digesting liquor in two respects.

It is preferred, according to one embodiment of the invention, to collect a withdrawn digesting liquor fraction—which has been displaced by replacement liquid without being mixed therewith—separately from a withdrawn digesting liquor fraction which has been mixed with the replacement liquid; in this manner, it is possible to utilize the heat contents of the withdrawn digesting liquor in a more economical and efficient manner. Thus, from the first such withdrawn fraction, being of high temperature, it is possible by lowering the pressure to obtain low-pressure steam which advantageously may be used for steaming or preheating the fiber material supplied to the digester; whereas the second withdrawn fraction, which is at too low a temperature for satisfactorily giving off usable steam, may be used for other heating purposes.

The invention will be more fully described hereinbelow with reference to the accompanying drawing which diagrammatically shows a continuous digesting plant to which the invention is applied.

In the drawing, the numeral 11 designates a steaming vessel in which wood chips or other comminuted cellulosic fiber materials supplied through a low-pressure charging apparatus 15, are heated by low pressure steam supplied through conduit 17, while the material is stirred and conveyed towards the outlet end of the steaming vessel by means of conveyor screw 19. These structures are all conventional, as will be understood.

A desired superatmospheric pressure, preferably about 1 atmosphere gauge, is maintained in vessel 11 as by means of an automatic control valve 21.

A suitable digesting liquor, for instance sodium lye, is supplied through the conduit 22. The mixture of chips and lye is transferred by means of a high-pressure charging apparatus 23 from the vessel 11 into a loop of circulating lye flushing the chips to the upper end of a standing cylindrical digester 25, as indicated. The chips are fed downwardly into the digester as by means of a motor-driven screw conveyor 27, and a large part of the lye is withdrawn through a cylindrical sieve 29 and by means of pump 31 is pumped through a heat exchanger 33, where it is heated. From there, the lye is returned to the charging apparatus 23 and carries chips charged into the same, with it to the digester

A further heating of the mixture of chips and lye is effected by means of a circulation system comprising two sieve girdles 35, 37 in the digester wall, a pump 39, a heat exchanger 41 and a return conduit 43 extending centrally in the digester and discharging, at about the center of the digester, the circulating lye taken out from the sieve girdles and heated in the heat exchanger 41. In the heat exchanger, the lye is heated to a temperature of approximately 170°C.

The sieve girdles 35, 37 may be of the type disclosed in U. S. Patent No. 2,695,232, and the disclosure of that patent is hereby incorporated herein by reference. A conventional valve 35a is shown for connecting the sieve girdles 35, 37 individually, or one at a time, to the pump 39, as indicated, and also as suggested in the aforesaid patent.

A hydraulic pressure of the order of 10 atmosphere gauge is maintained in the digester. During the slow and even downward movement of the fiber material through the digester, a reaction with the digesting liquor takes place, as is understood, so that the fiber material is completely digested when it reaches the lower end of the digester. There the material is fed down into a centrally located outlet 45 as by means of a motor-driven scraping or stirring device 47. Inserted in the conduit connected to the digester outlet is a throttling device 49 by means of which the material is conveyed into a blow tank 44 in which atmospheric pressure or a low superatmospheric pressure is maintained. The steam given off due to the pressure drop escapes through an outlet 46, whereas the pulp is discharged through a bottom outlet 48 and is carried through a conduit connected hereto, and in which a valve 50 controlled by the level of the blow tank is inserted, to the pulp vat 52 of a conventional rotary suction filter. On the rotary sieve drum 54 of said suction filter a pulp layer 56 is collected which is washed as by means of washwater, for instance, warm or cold fresh water supplied through conventional spray tubes 58. Part of the filtrate which consists of digesting liquor diluted with wash-water is collected in a container 60 from which it is returned through a conduit 51 to the digester to be used therein in accordance with the invention and in a manner to be described in more detail hereinafter.

Shown as being inserted in the digester wall at the lower end of the digester is a sieve girdle consisting of a perforated or slitted cylindrical sieve plate 53 arranged flush with the cylindrical wall of the digester, as disclosed in the aforesaid U. S. Patent No. 2695232. A space 55 for collection of sieved-off or withdrawn digesting liquor is arranged in a widened part of the digester wall exterior of said sieve plate. Said collecting space is shown as being connected by means of a conduit 57 to a steam separating device 59, preferably made as a cyclone, with the conduit 57 opening tangentially thereinto, as is understood.

The upper steam outlet of cyclone 59 is shown as being connected through the conduit 17 to the steaming vessel 11, and therefore, a comparatively low superatmospheric pressure is maintained in the cyclone 59. When the sieved-off or withdrawn digesting liquor enters the cyclone 59, gives off a great part of its heat content as steam which is used for heating the chips in the steaming vessel 11, as will be appreciated. The remainder of this withdrawn digesting liquor may be carried off at a reduced temperature through the outlet 61 and the conduit 62, in which a valve 63 controlled by the level of the cyclone 59 may be inserted, and, for example, to a plant for recovery of the chemicals.

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Adjacent to and below the sieve girdle 53, a second similar sieve girdle 68 is shown as being inserted in the digester wall. The space 70 for collecting digesting liquor in back of the sieve 68 is separated or hydraulically isolated from the space 55 and is shown as being connected by means of a conduit 72 to a second steam separating device which also preferably is made as a cyclone 74 having a tangential inlet of the conduit 72. The steam outlet of the cyclone 74 is connected to a condenser 76 in which the steam formed in the cyclone 74 is condensed and used, for instance, for producing warm water or for some other heating purpose, such as preheating the digesting liquor supplied to the digester through the conduit 22. The digesting liquor discharged through the bottom outlet of cyclone 74 is delivered by means of a pump 78 through a valve 80 controlled by the liquid level of the cyclone and through the conduit 82 to a plant for recovery of the chemicals of the digesting liquor. The cyclone 74 can be shut-off by means of the valves 84, 86 when there is no need to take steam out of the digesting liquor flowing through the conduit 72, or when the liquor temperature is so low that the steam given off is of practically no value. In such a case, by opening the valves 88, 90 said fraction of the digesting liquor can be carried to a container 92 from which it is pumped directly into the conduit 82, valve 80 also being controlled by the liquid level in container 92, as indicated. Thus, in said latter case the heat content of said second lye fraction is not utilized. If desired, the cyclone 74 can be omitted from the apparatus.

Shown as being inserted in the conduit 57 and 72 are conventional valves 94 and 96, respectively, which are suitably controlled in known manner by the quantity of liquid flowing thereto in such a manner as to maintain said quantity at a desired value.

The digesting liquor taken out through the sieve girdles 53, 68 is replaced by liquid taken from the container 60 by the conduit 51 and pumped into the digester by means of a high pressure pump 65. Connected to the pressure side of the pump is a vertically extending conduit 67 which penetrates the digester wall close to the upper end of the digester, as shown, and runs concentrically within the tube 43, preferably being suspended along the vertical center line or axis of the digester and having an open lower end at about the level of the sieve girdle 53. Preferably, the lower end of tube 67 is perforated, as shown.

Liquid pumped in through conduit 67 is distributed from the lower end thereof in the digester radially in all directions and displaces a corresponding quantity of digesting liquor. The digesting liquor, which is displaced by the discharge from the tube 67 in the digester and withdrawn through the sieve girdle 53 forms a first undiluted fraction having a substantially constant temperature and lye concentration. Farther downstream in the digester, the washing liquid supplied by tube 67 reaches the digester wall and consequently the digesting liquor taken out from the sieve girdle 68 is diluted or partially diluted and forms a second but dilnted lye fraction of a reduced temperature. By the separation of these two distinct fractions, it is possible to receive in the cyclone 59 a steam quantity corresponding to the temperature drop of the digesting liquor from practically the maximum cooking temperature of about 170°C. to about the steaming temperature 110°C., and simultaneously to have a very thorough displacement of the digesting liquor and a considerable temperature drop at the digester outlet. Diluting liquid is supplied through the conduit 67 preferably in such a quantity that the temperature at the outelt 45 is reduced to about 100° to 130°C. In as much as the lye concentration is simultaneously considerably reduced, there is no risk that the mechanical stresses exerted upon the pulp by the scraper 47 and the throttle valve 49 will cause any injurious or harmful attack upon the fibers, and the pulp will therefore be of optimum quality.

Instead of using the conduit 67, or in addition thereto, the replacement liquid can be supplied to the digester through a fluid distribution system or arrangement connected to the pump 65 and opening into the space between the sieve girdle 68 and the scraping and stirring device 47. Such a system is shown in the drawing as comprising an annular tube or fluid conduit 69 which is connected to a number of branch tubes 71 distributed around the digester and penetrating its wall, as indicated, with tube 69 being connected to the outlet of pump 65. The tubes 71 have orifices which are radially or somewhat tangentially disposed in the same direction relative to the digester wall and situated at some distance from the digester wall, as indicated. If desired, the quantity of liquid supplied through this system may be in excess of the quantity of digesting liquid withdrawn from the digester so that the pulp at the digester bottom will be diluted to a lower consistency, thereby facilitating its discharge through the outlet 45 and the throttle device 49.

The above-described embodiment is merely an example of an application of the invention, and it will be appreciated that the deails can be modified in various respects. Thus, the sieve girdles 53, 68 may be divided either along an axial plane or a transverse plane, only parts thereof being used at any given time and the connected parts being shifted periodically. Of course, the replacement liquid can be more or less pure water and the heat content of the withdrawn or sieved-off liquid can be utilized for purposes other than those mentioned above. If desired, the replacement liquid, referred to, may be supplied through an axial tube connected to the center of the rotary scraper 47 at the bottom of the digester. In case the amount of replacement liquid obtainable from the vessel 60 does not suffice for effecting a desired degree of cooling at the outlet end of the digester, an additional amount may be recirculated through a branch line connecting conduit 82 to conduit 51.

We claim :

1. A method of liberating cellulosic fiber material by digestion thereof with a digesting liquor at a raised pressure and a raised temperature in a continuous digester having an inlet and an outlet, said method being characterized in that a part of the digesting liquor is withdrawn from the fiber material immediately before the same passes out through the outlet of the digester, and in that said withdrawn digesting liquor is replaced by a weaker liquid at least a portion of which has previously passed through the digester outlet together with the fiber material.

2. A method according to Claim 1, characterized in that the replacement liquid consists of diluted digesting liquor preferably taken from a device for washing the fiber material after its digestion, for example, a wash filter.

3. A method according to Claim 1, characterized in that some of the withdrawn digesting liquor is undiluted while some of it is diluted by said weaker liquid, the diluted and undiluted withdrawn fractions being collected separately.

4. A method according to Claim 3, characterized in that the undiluted fraction of the withdrawn digesting liquor is at superatmospheric pressure and is subject, after being withdrawn, to a lower pressure giving off steam which is then used for steaming of the fiber material supplied to the digester.

5. Apparatus of the character described for continuously digesting cellulosic fiber material comprising : a digester having an inlet and an outlet disposed therebelow ; means for delivering fiber material and a digesting liquor to said digester through said inlet a washing device for the fiber material downstream from said digester; means for conveying fiber material from said digester outlet to said washing device; an agitating means arranged in said digester upstream from and adjacent to said outlet; means for withdrawing digesting liquor from the fiber material in said digester, at a point upstream from said agitating means; and means for conveying a mixture of digesting liquor and washwater from said washing device and into said digester at a point adjacent said point of withdrawal of said digesting liquor.

6. The apparatus defined in claim 5 wherein said digester is an upright cylindrical vessel and further wherein said last-named means includes a conduit extending vertically down along the axis of the digester and having an open bottom disposed approximately at the level at which said digesting liquor is withdrawn.

7. The apparatus defined in Claim 5 wherein said last-named means includes a conduit arrangement including a plurality of outlets distributed around the periphery of the digester and opening thereinto at a level between said agitating means and the point at which the digesting liquor is withdrawn from said digester.

8. The apparatus defined in Claim 5 wherein a steam separating device is connected to the means for withdrawing

digesting liquor and externally of the digester, said last-named device being at a lower pressure than said digester whereby steam will be given off therein, and means for utilising the steam given off in said separating device to pre-heat the fiber material being delivered to said digester.

9. The apparatus defined in Claim 8 wherein a second means for withdrawing digesting liquor is provided to withdraw such liquor from a point between said digester outlet and the first point of withdrawal of said liquor, and a second steam separating device being connected externally of said digester to said second means of withdrawing digesting liquor.

10. A method of liberating cellulosic fiber material by digestion thereof with a digesting liquor at a raised pressure and a raised temperature in a continuous digester having an inlet and an outlet, said method being characterized in introducing a weaker liquid centrally in said digester flowing cocurrently with said digesting liquor to displace at least a part of the same from the fiber material, withdrawing the displaced liquor from the digester immediately before the fiber material passes out through the outlet of the digester, some of the withdrawn digesting liquor being undiluted while some of it is diluted by said weaker liquid, separately collecting said diluted and undiluted withdrawn fractions, and discharging said fiber material through said outlet together with at least a portion of said weaker liquid, at least a portion of said weaker liquid having previously so passed through the digester outlet together with fiber material.

11. A method of liberating cellulosic fiber material by digestion thereof with a digesting liquor at a raised pressure and a raised temperature in a continuous digester having an inlet and an outlet, substantially as hereinbefore described with reference to the accompanying drawings.

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Dated this 23th day of December 1966.

MGIP Santh.—SL—38 Patent/62—6-3-63—100.

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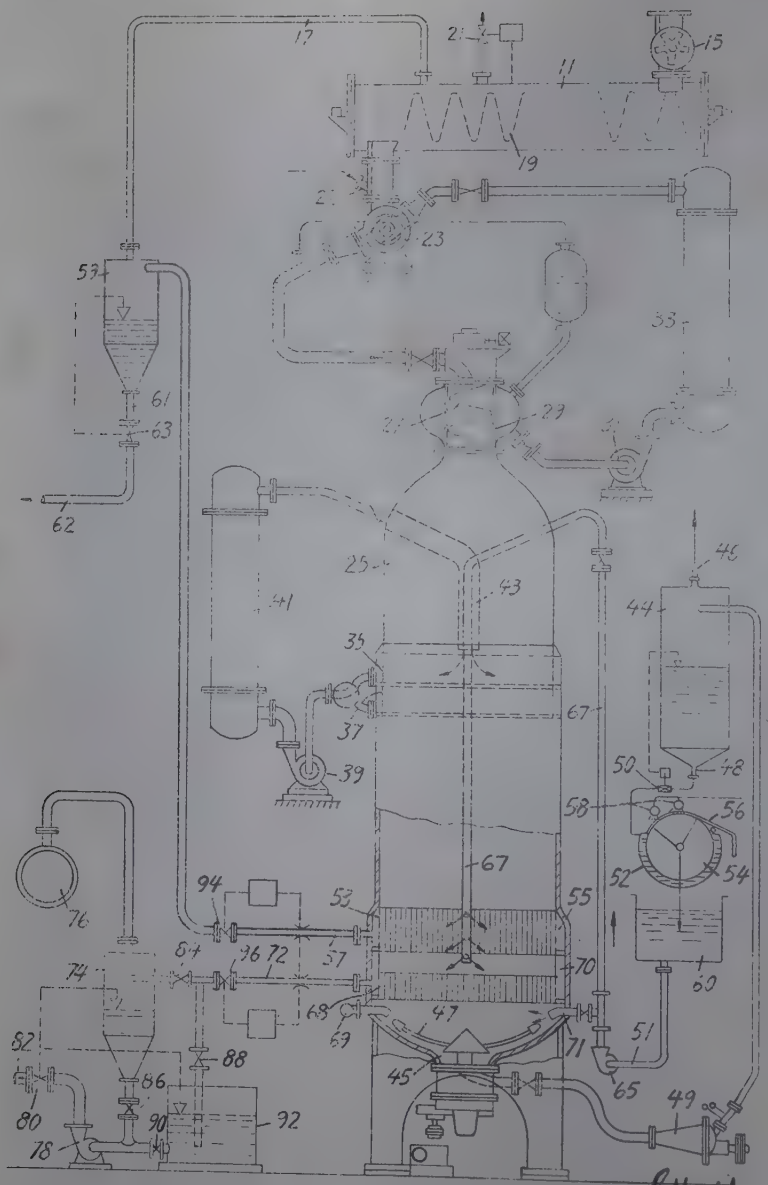
No. 74709 of 1960.



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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74710, filed 28th December 1960/ 7 Paus 1882 (Saka). (Accepted 2nd May 1962.)

REFRIGERATOR COMPARTMENT WALL.

GENERAL AMERICAN TRANSPORTATION CORPORATION, A CORPORATION OF THE STATE OF NEW YORK, U.S.A., HAVING A PLACE OF BUSINESS AT 135 SOUTH LA SALLE STREET, CITY OF CHICAGO, STATE OF ILLINOIS, U.S.A., MANUFACTURERS.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

The present invention relates to refrigerator cars, or the like ; and it is a general object of the invention to provide a refrigerator compartment wall of improved construction that has an exceedingly low coefficient of heat transfer and that is of strong and integral structure, as well as an improved method of making the same.

Another object of the invention is to provide a composite structural wall of improved construction that serves the structure into which it is incorporated as a supporting wall, as an outside or weather wall, and as a heat-insulating wall

Another object of the invention is to provide an improved method of making a composite structural wall of the character noted, wherein the wall may be erected or fabricated upon the site of the structure in which it is incorporated.

A further object of the invention is to provide an improved refrigerator compartment wall, and method of making the same, that involves a layer of synthetic organic resin that is molded *in situ* with respect to the other elements of the wall and that bonds together the other elements mentioned to produce an integral unified construction.

A further object of the invention is to provide an improved refrigerator compartment wall, and method of making the same, that involves a foamed layer of polyurethane, bonding together the other elements of the wall, and that is produced *in situ* upon curing of a corresponding mass of molding material that is injected into the spaces defined between the assembled other elements of the wall

A still further object of the invention is to provide a railway refrigerator car body of improved construction and arrangement, and method of making the same, wherein the car body comprises the assembly of only two principal subassemblies, each of integral and unitary structure, whereby the car body is of strong and rugged structure and is economical to manufacture.

Further features of the invention pertain to the arrangement of the elements of the refrigerator compartment wall and of the steps of the method of making the same, whereby the above-outlined and additional operating features thereof are attained.

The present invention, accordingly provides a refrigerator compartment wall of composite sandwich construction comprising rigid outer and inner sheets arranged in spaced-apart relation, two self-supporting heat-insulation layers arranged between said sheets and substantially completely filling the space therebetween, said two layers being respectively intimately bonded to said outer and inner sheets and also intimately bonded to each other, each of said layers being formed essentially of material of cellular structure and having a high compressive strength, and at least one of said layers being formed essentially of polyurethane.

Accordingly the present invention also provides the method of making a refrigerator compartment wall comprising providing a rigid outer sheet, providing a rigid inner sheet having a self-supporting slab of performed heat-insulating material of cellular structure intimately bonded to one surface thereof, arranging said sheets in adjacent spaced-apart relation with said slab therebetween and spaced from said outer sheet, and injecting a sufficient mass of foamed molding material into the space disposed between said slab and said outer sheet substantially completely to fill the same, wherein said molding material is of the polyurethane resin producing type, whereby upon curing of said mass there is produced *in situ* a foamed layer of such resin intimately bonded to said slab and to said outer sheet.

The invention, both as to its organization and method of operation, together with further objects and advantages thereof, will best be understood by reference to the following specification taken in connection with the accompanying drawing, in which:

Figure 1 is a perspective view of a railway refrigerator car embodying the present invention and made in accordance with the method thereof :

Figure 2 is an enlarged fragmentary lateral sectional view taken through the car of Figure 1 ; and

Figure 3 is a greatly enlarged fragmentary sectional view of the detail of construction of the side wall of the car body, taken in the direction of the arrows along the line 2-2 in Figure 2.

Referring now to the drawings, the refrigerator car 10 there illustrated and embodying the features of the present invention comprises a body including assembled complementary lower and upper sections or subassemblies 11 and 12 defining a lading compartment 13 therein. The lower body section 11 comprises a floor panel 14, two end wall panels 15 and two side wall panels 16, each of the side wall panels 16 having a substantially centrally disposed doorway formed therein that is provided with a pair of cooperating doors 17. The floor panel 14 comprises a lower supporting plate 18, formed of steel or the like, and carried by a center sill 19, also formed of steel or the like, which center sill 19 carries trucks, not shown, that are provided with track-engaging wheels.

The marginal edges of the supporting plate 18 are provided with upwardly directed flanges 20 ; and the end wall panels 15 and the side wall panels 16 are provided with outside sheaths 21, formed of steel or the like, that are welded or otherwise secured at the lower edges thereof to the flanges 20. Also, the abutting edges of the sheaths 21 are welded or otherwise secured together at the corners of the lower body section 11 to provide a water-tight box-like structure. Further elongated steel angle bars 22 are welded or otherwise secured to the upper edges of the sheaths 21 ; and also the abutting ends of the angle bars 22 are welded or otherwise secured together at the corners of the lower body section 11 to provide a fully reinforced structure. Each of the end panels 15 and each of the side panels 16 is reinforced by a plurality of upstanding spaced-apart structural members or side posts 23, the side posts 23 preferably being in the form of steel Z-bars ; the Z-bars 23 reinforcing each of the end panels 15 being arranged in laterally spaced-apart relation and interiorly of the associated sheath 21, and the Z-bars 23 reinforcing each of the side panels 16 being arranged in longitudinally spaced-apart relation and interiorly of the associated sheath 21. Of course, the Z-bars 23 are welded or otherwise rigidly secured to the associated sheath 21 for the reinforcing purpose. For example, as illustrated in Figure 3, the Z-bar 23 is disposed inwardly of the sheath 21 and provided with a web 24 having oppositely directed arms 25 at the opposite ends thereof, one of the arms 25 being welded or otherwise secured to the adjacent sheath 21. Also the lower ends of the Z-bars 23 project down into the inside of the adjacent flange 20 and are welded or otherwise secured thereto as to provide a reinforced structure extending from the supporting plate 18.

Also the floor panel 14 comprises lower and upper sheets 26 and 27 formed of a hard-surfaced material, such for example, as hardwood plywood, and an intervening layer 28 formed of material of rigid cellular structure, such for example, as a suitable foamed synthetic organic resin. Specifically, the layer 28 may be formed of foamed polystyrene. Accordingly, the floor panel 14 is of sandwhich construction, the sheets 26 and 27 being intimately

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bonded to the opposite surfaces of the layer 28. Moreover, the sheet 26 is arranged in direct engagement with the supporting plate 18 ; while the sheet 27 defines the floor of the lading compartment 13. This construction is very advantageous as the sheet 27 provides a hardwearing resilient floor for the lading compartment 13 ; the layer 28 is of exceedingly high compressive strength ; and the composite sandwich construction has an exceedingly low heat transfer factor.

The end wall panels 15 and the side wall panels 16 are of substantially indentical construction ; and as illustrated in Figures 2 and 3, the side wall panel 16 also comprises an inner sheet 29 formed of hard-surfaced material, such for example, as hardwood plywood, an inner layer 30 formed of material of rigid cellular structure, and an outer layer 31 formed of synthetic organic resin of cellular structure. The layer 30 is intimately bonded to the adjacent surface of the sheet 29 and engages the adjacent arms 25 of the side posts 23 ; while the layer 31 is intimately bonded to the adjacent surface of the sheath 21 and embeds the side posts 23. Also, the layer 31 is intimately bonded to the layer 30 at the meeting surfaces thereof. The layer 30 is formed of a suitable foamed synthetic organic resin, such, for example, as polystyrene ; while the layer 31 is formed of a suitable foamed polyurethane resin, such, for example, as a polyester cross-linked with urethane groups. Accordingly, the side panel 16 is of sandwich construction, the sheath 21 and the sheet 29 being intimately bonded to each other through the intermediary of the layers 30 and 31 that are intimately bonded to each other. Moreover, the sheet 29 defines one of the side walls of the lading compartment 13. This construction is very advantageous as the sheet 29 provides a hard-wearing resilient side wall for the lading compartment ; the layers 30 and 31 are of exceedingly high compressive strength ; and the composite sandwich construction has an exceedingly low heat transfer factor.

The upper body section 12 comprises two pitched roof sheaths 32 formed of steel, or the like, and welded or otherwise secured together at the longitudinally extending crest of the roof, and two structural triangular end sheaths 33 formed of steel, or the like, and welded or otherwise suitably secured to the roof sheaths 32 at the opposite ends thereof so as to provide a watertight inverted dish-like structure. Also, the upper body section 12 comprises a marginal flange surrounding the roof sheaths 32 and the end sheaths 33 and formed of steel structural members 34 that are substantially Z-shaped in cross-section, the eave edges of the roof sheaths 32 being supported upon the Z-bars 34 and welded or otherwise secured thereto, and the lower edges of the end sheaths 33 being welded or otherwise secured to the adjacent Z-bars 34 ; whereby a reinforced structure is provided. The roof sheaths 32 are reinforced by a plurality of laterally extending and longitudinally spaced-apart structural members or carlines 35, the carlines 35 preferably being in the form of steel Z-bars. The carlines 35 are disposed interiorly with respect to the roof sheaths 32 and one arm of each of the Z-bars 35 is welded or otherwise rigidly secured to the adjacent roof sheath 32 for the reinforcing purpose. Each of the carlines 35 comprises two sections, the upper ends of which are suitably welded or otherwise secured together, and the lower ends of which engage the associated Z-bars 34 and are welded or otherwise rigidly secured thereto, so as to provide a rigid reinforced structure.

Also the upper body section 12 comprises a ceiling sheet 36 formed of hard-surfaced material, such, for example, as hardwood plywood, an inner layer 37 formed of material of rigid cellular structure, and an outer layer 38 formed of synthetic organic resin of cellular structure. The layer 37 is intimately bonded to the adjacent surface of the sheet 36 and engages the lower portions of the adjacent arms of the carlines 35, the outer portions of the layer 37 being notched to receive the adjacent portions of the carlines 35, while the layer 38 is intimately bonded to the adjacent surfaces of the roof sheaths 32 and to the carlines 35. Also the layer 38 is intimately bonded to the layer 37 at the meeting surfaces thereof.

The layer 37 is formed of a suitable foamed synthetic organic resin, such, for example, as polystyrene ; while the layer 38 is formed of a suitable foamed polyurethane resin, such, for example, as a polyester cross-linked with urethane groups. Accordingly, the upper body section 12 is of sandwich construction, the sheet 36 and the roof sheaths 32 being intimately bonded to each other through the intermediary of the layers 37 and 38 that are intimately bonded to each other. Moreover, the sheet 36 defines the ceiling of the lading compartment 13. This construction is very advantageous as the sheet 36 provides a hard-wearing resilient ceiling for the lading compartment 13 ; the layers 37 and 38 are of exceedingly high compressive strength ; and the composite sandwich construction has an exceedingly low heat transfer factor.

In manufacturing the railway car 10, the lower and upper body sections 11 and 12 are separately fabricated and are then assembled to produce the finished car. In making the lower body section 11 : the supporting plate 18 is welded to the center sill 19 ; the side posts 23 are erected about the perimeter of the supporting plate 18 and welded thereto and to the flanges 20 ; the sheaths 21 are erected about the perimeter of the supporting plate 18 and welded to the side posts 23 and to the flanges 20 ; thereby producing the reinforced outer steel shell of the lower body section 11. The floor panel 14 may be built in sections that are subsequently placed upon the supporting plate 18 and secured together using ship-lap joints therebetween ; and more particularly, each section of the floor panel 14 is fabricated by intimately bonding the sheets 26 and 27 to the opposite surfaces of the preformed layer or slab 28 of foamed polystyrene, utilizing a suitable cement. The sections of the floor panel 14 are then placed in the lower car body 11 and secured together to provide the unified floor panel 14. In this arrangement, the opposite ends of the sections of the floor panel 14 engage the adjacent arms 25 of the side posts 23 ; whereby the opposite ends of the section of the floor panel 14 are spaced from the adjacent sheaths 21 by the webs 24 of the side posts 23, as illustrated in Figure 3. In the arrangement, the joints between the different sections of the floor panel 14 extend laterally across the car 10 from side to side thereof.

The end wall panels 15 and the side wall panels 16 are fabricated in a substantially identical manner in a plurality of sections that are subsequently placed within the car 11 upon the floor panel 14. More specifically, each of the side wall panels 16 comprises a plurality of sections that are separately fabricated ; and more particularly, the sheet 29 is intimately bonded to the adjacent surface of the preformed layer or slab 30 of foamed polystyrene utilizing a suitable cement.

The sections of the side wall panel 16 are then placed in the lower car body 11 upon the floor panel 14 and adjacent to the side posts 23 so that the sheet 29 faces the interior of the lading compartment 13 and so that the exposed surface of the slab 30 engages the flanges 25 provided upon the car post 23. The plurality of sections of the side wall panel 16 are thus assembled and secured together utilizing ship-lap joints therebetween so as to produce the composite side wall panel 16. Of course, at this stage of the assembly the sections of the side wall panel 16 must be suitably blocked in place from the interior of the compartment 13, as they are not otherwise secured to the side posts 23. The assembly of the end wall panels 15 proceeds in the manner of the side wall panels 16, as described above ; whereby the floor and the two end walls and the two side walls of the lading compartment 13 are thus defined.

At this time, the foamed molding material that is productive of the polyurethane resin upon curing is injected under pressure into the spaces disposed about the perimeter of the end wall panels 15 and the side wall panels 16 so as substantially completely to fill these spaces embedding the side posts 23. For example, with respect to the side wall panel 16, the foamed molding material produces upon curing the layer 31 of polyurethane resin that is intimately bonded to the side posts 23, to the adjacent sheath 21 and to the adjacent surface of the slab 30, the layer 31 extending down between the flange

20 and the adjacent end of the floor panel 14 and bonded to the adjacent ends of the elements 26, 27 and 28. After curing of the polyurethane resin, the blocking structure may be removed from the interior of the lading compartment 13, as the end wall panels 15 and the side wall panels 16 are now intimately bonded to each other and to the floor panel 14 ; whereby the lower body section 11 is finished and ready for assembly with respect to the upper body section 12.

In making the upper body section 12, the roof sheaths 32, the end sheaths 33 and the Z-bars 34, together with the carlines 35 are suitably welded together to provide the substantially pan-like steel shell thereof. The ceiling panel is also fabricated into a number of sections that are ultimately introduced into the upper body section 12 and secured together employing ship-lap joints therebetween. More particularly, each section of the ceiling panel is produced by securing the sheet 36 to the adjacent surface of the preformed foamed layer or slab 37 of polystyrene employing a suitable cement. Laterally spaced-apart notches are formed in the opposite ends of the slab 37 to receive the carlines 35 ; and then the sections of the celing panel are introduced into the shell of the upper body section 12 and secured together. At this time, the foamed molding material that is productive of the polyurethane resin upon curing is injected under pressure into the space disposed between the slab 37 and the shell of the upper body section 12 and between the carlines 35 so as substantially completely to fill the space and to embed the carlines ; whereby upon curing of the polyurethane resin the layer 38 is produced that is intimately bonded to the roof sheaths 32, to the end sheaths 33, to the carlines 35 and to the adjacent surfaces of the slab 37, including the surfaces of the notches formed therein. The ends of the layer 38 extends into contact with the Z-bars 34 and are bonded thereto producing an integral construction of the upper body section 12.

Thereafter the upper body section 12 is inverted and placed upon the lower body section 11 so that the flanges of the Z-bars 34 rest upon the flanges of the angle bars 22, and are suitably welded in place. Before welding of the adjacent flanges provided on the members 34 and 38, a suitable cement may be placed upon the elements 36 and 38 disposed about the perimeter of the Z-bars 34 so that these parts are cemented to the ends of the engaged elements of the end wall panels 13 and the side wall panels 16. For example, with reference to the side wall panel 16, the ends of the elements 29 and 30 may be cemented to the adjacent surface of the element 36 and the end of the elment 31 may be cemented to the adjacent surface of the element 38. Accordingly, at this time, a unitary car body is produced of the separately fabricated body sections 11 and 12 ; and in the construction of the railway car 10, the engaging insulating panels are intimately bonded to each other so as to produce in effect a single unified insulating lining for the composite steel shell of the railway car 10 and bounding the lading compartment 13.

The fabrication of the doors 17 that are provided in the doorways formed in the side wall panels 16 is substantially the same as that of the sections of the side wall panels 16, as described above ; whereby the description of these steps is omitted in the interest of brevity. Of course, these separately fabricated doors 17 are hung and arranged when closed properly to seal the doorways formed in the side wall panels 16, in the usual manner.

Reconsidering the molding of the polyurethane resin layers 31, 38, it is pointed out that a large variety of molding materials may be employed, as the system is predicated upon the reaction of polyisocyanate and water to liberate carbon dioxide, while simultaneously the polymerization and cross-linking reactions between the polyisocyanate and the polyester entrap the liberated carbon dioxide ; whereby no external blowing or foaming agent is required. Moreover, the resin is self-curing, since the reactions are exothermic and take place at room temperature. When the ingredients are mixed employing some water, the reactions are initinted producing the carbon dioxide gas and the resulting foam ; however, suitable catalyst (amines) are ordinarily added to the ingredients to accelerate the reactions and to reduce the curing time. For example, the curing time of a typical molding material can be reduced from about ten hours to about one to two hours by the addition of an appropriate amount of urea. Also the polyesters (alkyd resins) and the polyisocyanates should be selected so as to control the density of the resulting polyurethane resin, as a rigid (or at least a semi-rigid) foamed structure is desired in the present case. Fortunately, the density of the polyurethane resin may be controlled over a wide range from about 1·5 to about 40 pounds per cubic foot by controlling the amount of water employed, the amount of catalyst added, and particularly by selecting the polyisocyanate used for cross-linking ; and in general, it is noted that the diisocyanates produce linear polymers of relatively low density and rigidity, while the triisocyanates and higher polyisocyanates produce more highly cross-linked polymers of relatively high density and rigidity. In the present case, a suitable polyurethane resin (condensation product) may be produced that is formed essentially of copolymers of a polybasic carboxylic acid such as adipic acid and a polyhydric alcohol such as glycerol cross-linked with naphthyldiisocyanate and some diphenoltriisocyanate.

These polyurethane resins are highly desirable in the present case because of the great compressive strength, the high tensile strength, the high impact resistant characteristic, and the exceedingly low heat transfer factor thereof, together with the circumstance that they are self-curing at room temperature and may be readily molded *in situ*, so as substantially completely to fill all of the space into which the foamed molding material is injected. The complete elimination of air pockets or spaces in the heat-insulating wall is very advantageous as it prevents the circulation of convection air currents therein, with the result that the co-efficient of heat trasfer of the heat-insulating wall is greatly reduced. Moreover, these resins being of the thermosetting type can withstand temperature up to 350°F., without damage thereto, which gives ample margin for any high-temperature conditions that may exist immediately adjacent to the sheaths of the wall panels, when the refrigerator car is in daytime use in certain desert areas of this country in the summer months. Furthermore, these resins possess the peculiar characteristic of forming tenacious bonds with almost any kind of material in contact therewith during the curing reactions, and including steel, wood, and other resins ; whereby the structural strength of the car is increased by the distribution or spreading of the bulge stress on the sheaths thereof.

In view of the foregoing, it is apparent that there has been provided a refrigerator compartment wall of improved construction and arrangement, that is of unitary sandwich construction, exceedingly strong, and characterized by an exceedingly low heat transfer factor, as well as a railway refrigerator car provided with such walls and also an improved method of making the walls.

In the appended claims, it is intended that the expression "refrigerator compartment wall" shall embrace any wall thereof, including a floor wall and a ceiling wall and a door wall thereof, as the end wall and the side wall thereof.

While there has been described what is at present considered to be the preferred embodiment of the invention, it will be understood that various modifications may be made therein, and it is intended to cover in the appended claims all such modifications as fall within the true spirit and scope of the invention.

We claim:

1. A refrigerator compartment wall of composite sandwich construction comprising rigid outer and inner sheets arranged in spaced-apart relation, two self-supporting heat-insulating layers arranged between said sheets and substantially completely filling the space therebetween, said two layers being respectively intimately bonded to said outer and inner sheets and also intimately bonded to each other, each of said layers being formed essentially of material of cellular structure and having a high compressive strength, and at least one of said layers being formed essentially of polyurethane.

2. The wall construction according to Claim 1, wherein said outer and inner sheets are formed essentially of steel and wood, respectively.

3. The wall construction according to Claim 2, wherein said one layer is intimately bonded to said outer sheet.

4. A refrigerator compartment wall according to Claim 1, 2, or 3, wherein each of said layers is formed essentially of synthetic organic resin, and at least one of said layers is formed essentially of a polyester cross-linked with urethane groups, said layers forming the only connection between said outer and inner sheets.

5. A refrigerator compartment wall according to any of Claims 1 to 4, wherein one of said layers is formed essentially of polystyrene and the other of said layers is formed essentially of polyurethane.

6. A refrigerator compartment wall according to any of Claims 1 to 5, wherein at least one of said layers is formed essentially of copolymers of a polybasic carboxylic acid and a polyhydric alcohol cross-linked with a polyisocyanate, said one layer being in direct surface-to-surface contact with the other layer and one of said sheets.

7. A refrigerator compartment wall according to any of Claims 1 to 5, wherein at least one of said layers is formed essentially of copolymers of adipic acid and glycerol cross-linked with naphthyldiisocyanate, said one layer being in direct surface-to-surface contact with the other layer and one of said sheets.

8. A refrigerator compartment wall according to any of the preceding claims, wherein said outer and inner sheets are formed essentially of metal and plywood, respectively, said outer layer being separated from said inner sheet by the thickness of said inner layer, said inner layer being separated from said outer sheet by the thickness of said outer layer.

9. A refrigerator compartment wall according to Claim 8, wherein said outer layer comprises an *in situ* formed mass of foamed polyurethane and said inner layer comprises a preformed slab of foamed polystyrene.

10. A refrigerator compartment wall according to Claim 1, including a number of structural reinforcing members arranged between said sheets and disposed in spaced-apart relation with respect to each other, said members being secured to said outer sheet and spaced from said inner sheet, a self-supporting heat-insulating slab arranged between said sheets and intimately bonded to said inner sheet and engaging said members, said slab being formed essentially of material of cellular structure and having a high compressive strength, and a self-supporting heat-insulation layer arranged between said sheets and intimately bonded mutually to said outer sheet and to said members and to said slab, whereby the space between said sheets is substantially completely filled by said members and said slab and said layer, said layer being formed essentially of a polyurethane resin of cellular structure and having a high compressive strength.

11. A refrigerator compartment wall according to Claim 10, wherein said self-supporting heat insulating slab is spaced inwardly from said outer sheet, said self-supporting heat-insulating layer is spaced outwardly from said inner sheet and embedding said members, said slab and said layer engaging each other and intimately bonded together and cooperating with said members to fill the space between said sheets, said slab being separated from said outer sheet by the thickness of said layer being separated from said inner sheet by the thickness of said slab.

12. A refrigerator compartment wall according to Claim 1, having supports arranged between the outer and inner sheets and embedded in the polyurethane layer of heat-insulating material.

13. The method of making a refrigerator compartment wall comprising providing a rigid outer sheet, providing a rigid inner sheet having a self-supporting slab of preformed heat-insulating material of cellular structure intimately bonded to one surface thereof, arranging said sheets in adjacent spaced-apart relation with said slab therebetween and spaced from said outer sheet, and injecting a sufficient mass of foamed molding material into the space disposed between said slab and said outer sheet substantially completely to fill the same, wherein said molding material is of the polyurethane resin producing type, whereby upon curing of said mass there is produced *in situ* a foamed layer of such resin intimately bonded to said slab and to said outer sheet.

14. The method according to Claim 13, wherein the material of said slab consists essentially of foamed synthetic organic resin.

15. The method according to Claim 13 or 14, including said rigid outer sheet having a plurality of spaced-apart structural reinforcing members securely fastened to one surface thereof, and said foamed layer of said resin embedding said members and intimately bonded thereto and also intimately bonded to said slab and to said outer sheet.

16. The method of making a refrigerator compartment wall for a refrigerator car comprising providing an underframe, securing a heat-insulating floor to the upper surface of said underframe, erecting an upstanding outer shell including internal side posts upon said underframe, providing a multi-section inner liner, wherein each section of said liner includes a hard-surfaced inner sheet carrying a self-supporting slab of preformed heat-insulating material, of cellular structure intimately bonded to one surface thereof, erecting said multi-section inner liner within said outer shell and upon said floor so that said inner sheets cooperate to define a lading compartment within said inner liner and so that said slabs engage the adjacent side posts with said inner sheets spaced from said outer shell, and injecting masses of foamed molding material in the space disposed between said slabs and said outer shell and substantially completely filling the same, wherein said molding material is of the polyurethane resin producing type, whereby upon curing of said masses there are produced *in situ* foamed layers of such resin embedding said side posts and intimately bonded thereto and also intimately bonded to said slabs and to said outer shell.

17. The method of making a refrigerator compartment wall for a refrigerator car roof comprising providing an outer shell including internal carlines, providing a ceiling including a hard-surfaced inner sheet carrying a self-supporting slab of preformed heat-insulating material of cellular structure intimately bonded to one surface thereof, arranging said outer shell and said ceiling in adjacent spaced-apart relation with said carlines and said slab in engagement with each other, and injecting a sufficient mass of foamed molding material into the space disposed between said slab and said outer shell and substantially completely filling the same, wherein said molding material is of the polyurethane resin producing type, whereby upon curing of said mass there is produced *in situ* a foamed layer of such resin embedding said carlines and intimately bonded thereto and also intimately bonded to said slab and to said outer shell.

18. A refrigerator compartment wall constructed substantially as herein described with reference to the accompanying drawings.

19. A method of making a refrigerator compartment wall substantially as herein described with reference to the accompanying drawings.

20. A refrigerator car embodying the compartment wall defined in any of Claims 1 to 12 or 18.

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Agent for the Applicants.

Dated this 28th day of December 1960.

MGIP South.—SL—18 Patent/62—22-3.63—100

GENERAL AMERICAN TRANSPORTATION CORPN.
No. 74710 of 1960.

FIG. 1

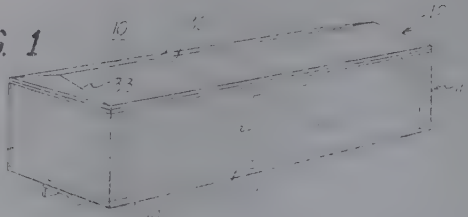


FIG. 2

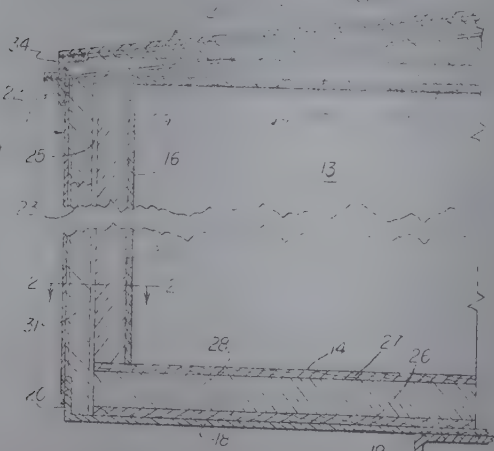
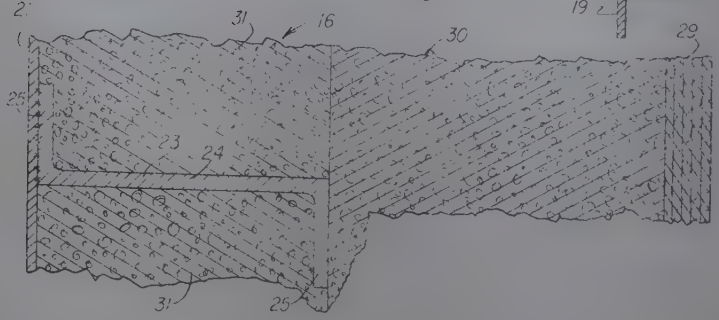


FIG. 3



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(Accepted 12th June 1962.)

"PREFABRICATED HEAT-INSULATING WALL SECTION"

GENERAL AMERICAN TRANSPORTATION CORPORATION, A CORPORATION OF THE STATE OF NEW YORK, U. S. A., HAVING A PLACE OF BUSINESS AT 135 SOUTH LA SALLE STREET, CITY OF CHICAGO, STATE OF ILLINOIS, U. S. A. MANUFACTURERS.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

The present invention relates to prefabricated heat-insulating wall sections and to methods of making the same.

It is the general object of the present invention to provide a composite heat-insulating liner defining a substantially box-like volume or space that is to be refrigerated.

Another object of the invention is to provide a heat-insulating liner difining a refrigerated compartment and comprising a plurality of walls, each wall including a number of prefabricated wall sections of sandwich structure and of improved construction and arrangement.

A further object of the invention is to provide a prefabricated heat-insulating wall section of sandwich structure that is of improved and simplified construction and arrangement.

A still further object of the invention is to provide a method of making a heat-insulating wall section of the character described and involving a minimum number of steps that may be readily carried out in a simple and economical manner.

Further features of the invention pertain to the arrangement of the elements of the wall section and of the steps of the method of making the same, whereby the above-outlined and additonal operating features thereof are attained.

In accordance with the present invention there is provided a prefabricated heat-insulating wall section of sandwich structure comprising a core formed essentially of formed polystyrene, and a pair of outer sheets each formed essentially of plywood and respectively cemented to the opposite faces of said core ; said care being of composite construction including a number of individual block-like slabs cemented together in abutting edge relationship ; each of said outer sheets being of composite construction including a plurality of individual panels cemented together in abutting edge relationship, and a plurality of elongated ribbon like metal splines arranged mutually in aligned grooves respectively provided in the abutting joined edges of said panels, the slabs in said core being staggered with respect to the panels in said outer sheets so that the joints in said core are arranged in non-coinciding relationship with respect to the joints in said outer sheets through the thickness of said wall section.

Accordingly the present invention also provides the method of making a heat-insulating wall section, comprising fabricating a pair of outer sheets each formed essentially of plywood, each of said outer sheets including a plurality of individual panels cemented together in abutting edge relationship and a plurality of elongated ribbon-like metal splines arranged mutually in aligned grooves respectively provided in the abutting joined edges of said panels providing a plurality of individual block-like slabs each formed essentially of foamed polystyrene, producing a sandwich structure of said outer sheets and a number of said slabs arranged as a composite core therebetween, wherein said slabs in said core are arranged in abutting edge relationship with each other and with moisture-impervious adhesive layers respectively disposed between the abutting joined edges of said slabs and with moisture-impervious adhesive layers respectively disposed between the faces of said core and the adjacent inner surfaces of said outer sheets, and then subjecting said sandwich structure to pressure by passing the same through a pair of cooperating pressure rollers.

The invention, both as to it organization and method of operation, together with further objects and advantages thereof, will best be understood by reference to the following specification, taken in connection with the accompanying drawing, in which :

Figure 1 is a front perspective view of a railway refrigerator car provided with a lading compartment defined by a heat-insulating lining embodying the present invention ;

Figure 2 is an enlarged fragmentary lateral sectional view taken through the top of the refrigerator car adjacent to one end thereof, along the line 2-2 in Figure 1, and illustrating a portion of the lining defining the refrigerated lading compartment of the railway car ;

Figure 3 is a plan view of one of the heat-insulating wall sections incorporated in the lining mentioned ;

Figure 4 is a top view of the wall section of Figure 3 ;

Figure 5 is a bottom view of the wall section of Figure 3 ;

Figure 6 is an end view of the wall section of Figure 3 ;

Figure 7 is a greatly enlarged fragmentary sectional view, taken in the direction of the arrows along the line 7-7 in Figure 3, and illustrating one of the joints in the wall section ;

Figure 8 is an exploded prespective view of the elements forming the composite wall section of Figure 3 ; and

Figure 9 is a fragmentary view of a rolling machine that is employed in a step of the mujacture of the wall section.

Referring now to Figures 1 and 2 of the drawing, there is illustrated a railway refrigerator car 10 that comprises a steel outer shell 11 of generally box-like configuration and provided with a composite interior heat-insulating liner 12 embodying the features of the present invention. More particularly, the composite liner 12 comprises a pair of side walls 13, a pair of end walls 14, a floor wall, not shown, and a ceiling wall 15; and the walls mentioned cooperate to define a lading compartment 16 that is cooled by associated refrigerating apparatus, not shown. Preferably, the walls 13, 14, 15, and including the floor wall, if desired, are of substantially identical sandwich construction and are suitably joined together and to the respectively adjacent walls of the steel outer shell 11 so as to provide a rigid structure and to produce the composite heat-insulating liner 12 bounding the refrigerated lading compartment 16. Each of the walls 13, 14, 15, and including the floor wall, if desired, comprises a plurality of prefabricated heat-insulating wall sections 20 of the construction and arrangement illustrated in Figures 3 to 8, inclusive; and in each of the said walls the individual wall sections 20 are suitably joined together to provide a composite and continuous wall, the joints between the individual wall sections 20 being produced in any suitable manner, as by cementing. Specifically, the adjacent edges of the

wall sections 20 may be arranged in abutting relationship and secured together utilizing a suitable water impervious cement, such, for example, as an epoxy resin.

Referring now to Figures 3 to 8, inclusive, each of the wall sections 20 is of sandwich structure comprising a core 30 formed essentially of foamed polystyrene and a pair of outer sheets 40 and 50 each formed essentially of plywood and respectively cemented to the opposite faces of the core 30. The core 30 is of composite construction, including a number of individual block-like slabs 31 cemented together in abutting edge relationship. The outer sheet 40 is also of composite construction including a plurality of individual panels 41 cemented together in abutting edge relationship, and a plurality of elongated ribbon-like metal splines 42 arranged in mutually aligned grooves respectively provided in the abutting joined edges of the panels 41, as best shown in Figure 7. Further, the outer sheet 50 is also of composite construction and identical in construction to that of the outer sheet 40, the individual panels in the outer sheet 50 being designated 51.

As a constructional example and referring to Figures 3 to 7, inclusive, the block-like wall section 20 may have a length in the x direction of 20 feet and a width in the y direction of 10 feet and a thickness in the z direction of 6 3/4 inches. The outer sheet 40 comprises a top row of two full panels 41 extending in the x direction of the wall section 20, and a bottom row of one full panel 41 and two half panels 41 extending in the x direction of the wall section 20; wherein each of the full panels 41 has a length of 10 feet and a width of 5 feet, and each of the half panels 41 is square having a side of 5 feet. The outer sheet 50 comprises a top row of one full panel 51 and two half panels 51 extending in the x direction of the wall section 20, and a bottom row of two full panels 51 extending in the x direction of the wall section 20; wherein the dimensions of each full panel 51 correspond to the dimensions of each full panel 41, and the dimensions of each half panel 51 correspond to the dimensions of each half panel 41. Accordingly, the panel 41 in the outer wall 40 are staggered with respect to the panels 51 in the outer wall 50, so that in the composite wall section 20, at least the vertical joints in the outer sheets 40 and 50 are arranged in non-coinciding relationship with respect to each other through the thickness of the wall section 20. Each of the outer walls 40 and 50 has a thickness of 3/8 inch. Each of the panels 41 and 51 may be formed of 3/8 inch fir plywood that is preferably treated with an agent rendering the same moisture-resistant; the panels 41 illustrated in Figure 7 being indicated as of 3-ply. Each of the splines 42 may be formed of a ribbon-like steel strap 1/8 inch × 1/2 inch.

The core 30 comprises five individual slabs 31, each of which slabs 31 has a length in the y direction of the wall section 20 of 10 feet and a width in the x direction of the wall section 20 of 2 feet and a thickness in the z direction of the wall section 20 of 6 inches. Accordingly, the vertical joints in the core 30 are stagged with respect to the joints in the outer sheets 40 and 50 and are thus arranged in non-coinciding relationship with respect thereto through the thickness of the wall section 20. Each of the slabs 31 may comprise "Styrofoam No. 22", manufactured by Dow Chemical Company, that essentially comprises foamed polystyrene that is impregnated with an agent rendering the same fire-resistant in the sense that it is self-extinguishing with respect to flame. This material has a density of approximately 2 pounds per cubic foot and a very low K-factor of about 0.27 B.T.U /foot²/hour/°F. /inch, and is commonly referred to as rigid expanded cellular synthetic resin having closed cells that are independent and hermetically sealed with respect to each other so that it is also moisture-resistant.

In the outer sheet 40 (and likewise in the outer sheet 50), the adjacent panels 41 are secured together in abutting edge relationship and to the steel splines 42 arranged mutually in the aligned grooves respectively provided in the abutting joined edges of the panels 41 utilizing any suitable moisture-impervious cement, such, for example, as an epoxy resin. Similarly, the adjacent abutting edges of the slabs 31 are secured together to form the composite core 30 utilizing a suitable water-impervious cement; and likewise, the outer sheets 40 and 50 are secured to the respectively adjacent surfaces of the core 30 utilizing a suitable water-impervious cement. A number of such water-impervious cements (including the epoxy resins) are available on the market; however, it is preferable to utilize the water-emulsion glue, for the purposes mentioned, that is manufactured by the Heveatex Corporation at Melrose, Massachusetts, since this glue (or cement) is easy to handle and setsup quickly in air at room temperature providing a strong adhesive bond between the individual slabs 31 and between the the composite core 30 and the adjacent surfaces of the outer sheets 40 and 50. Actually, the water-impervious cement mentioned provides exceedingly thin layers between the adjacent abutting edges of the individual slabs 30 and between the surfaces of the composite core 30 and the respective adjacent surfaces of the outer sheets 40 and 50; which layers have not been illustrated in the drawing by virtue of the scale involved, since the thicknesses of these layers are only a matter of several thousandths of an inch.

Considering now the method of making the wall sections 20 in accordance with the present invention, the outer sheets 40 and 50 are suitably fabricated, and actually the outer sheets 40 and 50 are identical. Thereafter, to the inner surface of the outer sheet 50, there is applied a suitable layer or coating of the previously mentioned adhesive. Shortly following the application of the coating of adhesive to the inner surface of the outer sheet 50, the applied coating becomes tacky; whereupon, the preformed foamed polystyrene slabs 31 are applied thereto. As the slabs 31 are applied to the adhesive coating carried by the inner surface of the outer sheet 50, the adjacent abutting edges thereof are suitably coated with this adhesive, so that a layer or coating of this adhesive is carried in the joint between the abutting edges of each two of the slabs 31. Of course, the slabs 31 are applied to the coating carried by the inner surface of the outer sheet 50 running in the y direction of the ultimate wall section 20, as previously explained, and as indicated generally in Figure 8. Then, a layer or coating of this adhesive is applied to the inner surface of the outer sheet 40; and after the adhesive coating becomes tacky, the outer sheet 40 is placed upon the composite core 30 with the tacky coating in contact therewith, so as to produce a composite sandwich structure.

Thereafter, the assembly is transferred to a pressure rolling machine that is provided with a pair of substantially horizontally disposed and vertically aligned pressure rolls 60, as illustrated in Figure 9. The machine is operated, in order to cause the assembled sandwich structure to be fed therethrough and between the revolving rolls 60, the rolls 60 being adjusted so as to exert a pressure therebetween upon the assembly in the general range 25 to 50 pounds per square inch; this rolling operation compacting the assembly, while at room temperature, into the desired final form, producing the wall section 20, as shown in Figures 3 to 6, inclusive. In passing, it is noted that while the outer sheets 40 and 50 are identical, as a matter of construction, the outer sheets 40 and 50 are assembled in an inverted direction with respect to each other in producing the sandwich structure and preceding the final rolling operation, described above, so that the vertical joints in the respective outer sheets 40 and 50 are arranged in non-coinciding relationship with respect to each other through the thickness of the wall section 20. This rolling step sizes the wall section 20 with respect to the thickness thereof, insures intimate bonding between the individual slabs 31 of the core 30 and intimate bonding of the composite core 30 to the respective outer

sheets 40 and 50, minimizes air bbles, or other vids in the layers of cement involved, and insures slight compacting of the cellular material of the composite core 30 in the finished wall section 20.

The prefabricated heat-insulating wall section 20 of the construction described is very advantageous in the subsequent production or building of heat-insulated enclosures, particularly refrigerated space enclosures, since they are of exceedingly light weight and may be readily handled and fitted together by hand, without the necessity of utilizing hoisting or other handling equipment, The wall section 20 is characterized by a low K-factor of about 0.27, as previously noted; and either of the outer sheets 40 or 50 of the composite sandwich structure 20 may be arranged to provide the interior wall of the refrigerated space 16 defined by the ultimately produced composite lining 12. The wall sections 20 are highly moisture-resistant and are substantially vermin-proof. Moreover, the wall sections 20 are very rigid and strong, having both substantial tensile strength and exceedingly high compressive strength, thereby rendering the wall sections 20 particularly useful in producing the floor wall of the defined refrigerated enclosure, since the floor wall thus produced is capable of withstanding substantial loading stresses without undesirable deformation thereof. Further, the wall sections 20 are highly resistant to warping and to age diterioration; whereby they are characterized by permanence and shape-retention after long and severe service.

While the doors, or other required closure members, that are normally provided in the composite lining 12 in order to afford access into the refrigerated lading space or compartment 16, have not been illustrated as a matter of structure, it will be understood that the may be readily fabricated in any suitable manner, utilizing the wall sections 20, since the wall sections 20 may be readily cut with an ordinary handsaw to the required dimensions for use, as required. Further, it will be appreciated that the wall sections 20 may be fabricated in a required range of sizes, so as to minimize the cutting and fitting thereof into the ultimate constructions.

While the composite lining 12 has been disclosed as being arranged within the interior steel shell 11 of the railway refrigerator car 10, it will be appreciated that this composite lining 10 may be readily constructed in other forms of outer shells made of wood, masonry, etc., for the purpose of providing the desired enclosed refrigerated space or enclosure within the outer building shell, and without reference to the particular construction or composition of the outer building shell.

In view of the foregoing, it is apparent that there has been provided an improved heat-insulating lining defining a refrigerated space or compartment and comprising a plurality of walls, each wall including a number of wall sections of sandwich structure and of improved construction and arrangement; and also there has been provided an improved method of making a heat-insulating wall section of the character described, involving a minimum number of simple steps that may be carried out in a ready and economical manner.

While there has been described what is at present considered to be the preferred embodiment of the invention, it will be understood that various modifications may be made therein, and it is intended to cover in the appended claims all such modifications as fall within the true spirit and scope of the invention.

WE CLAIM :—

1. A prefabricated heat-insulating wall section of sandwich structure comprising a core formed essentially of foamed polystyrene, and a pair of outer sheets each formed essentially of plywood and respectively cemented to the opposite faces of said core; said core being of composite construction including a number of individual block-like slabs cemented together in abutting edge relationship; each of said outer sheets being of composite construction including a plurality of individual panels cemented together in abutting edge relationship, and a plurality of elongated ribbon-like metal splines arranged mutually in a igned grooves respectively provided in the abutting joined edges of said panels; the slabs in said core being staggered with respect to thepanels in said outer sheets so that the joints in said core are arranged in non-coinciding relationship with respect to the joints in said outer sheets through the thickness of said wall section.

2. The prefabricated heat-insulating wall section according to claim 1, wherein each of said slabs is impregnated with an agent rendering the same fire-resistant, and wherein each of said panels is impregnated with an agent rendering the same moisture-resistant.

3. A prefabricated heat-insulating wall section according to claim 1, wherein two moisture-impervious adhesive layers respectively are arranged between the opposite faces of said core and the adjacent inner surfaces of said outer sheets and adhering said core and said outer sheets in assembled relationship.

4. A prefabricated heat-insulating wall section according to claim 1, wherein the panels in each of said outer sheets are staggered with respect to the panels in the other of said outer sheets so that at least some of the joints in said outer sheets are arranged in non-coinciding relationship with each other through the thickness of said wall section.

5. A prefabricated heat-insulating wall section of sandwich structure comprising a core formed essentially of foamed polystyrene, and a pair of outer sheets each formed essentially of polywood and respectively cemented to the opposite faces of said core, said wall section being of block-like configuration having a length (X) and a width (Y) and a thickness (Z); said core being of composite construction including a number (N) of individual block-like slabs cemented together in abutting edge relationship; each of said slabs extending in the y direction of said wall section and having a length of substantially Y and a width of substantially X/N and a thickness of at least 75% Z; each of said outer sheets being of composite construction including a plurality of individual panels cemented together in abutting edge relationship, and a plurality of elongated ribbon-like metal splines arranged mutually in aligned grooves respectively provided in the abutting joined edges of said panels ; the panels in each of said outer sheets being staggered with respect to the panels in the other of said outer sheets so that at least some of the joints in said outer sheets are arranged in non-coinciding relationship with each other through the thickness of said wall section.

6. A prefabricated heat-insulating wall section according to claim 5, wherein the panels in each of said outer sheets extend in the x direction of said wall section and have a length in the rage X/4 to X/2 and a width of substantially Y/2 and a thickness not in excess of about 10% Z.

7. A prefabricated heat-insulating wall section for a substantially box-like refrigerated volume comprising a plurality of said wall sections secured together in abutting edge relationship; each of said wall sections being of sandwich structure comprising a core formed essentially of foamed polystyrene, an inner sheet formed essentially of plywood and cemented to the inner face of said core, and an outer sheet formed essentially of plywood and cemented to the outer face of said core, said core being of composite construction including a number of individual block-like slabs cemented together in abutting edge relationship, each of said sheets being of composite construction including a plurality of individual panels cemented together in abutting edge relationship and a plurality of elongated ribbon-like metal splines arranged mutually in aligned grooves respectively provided in the abutting joined edges of said panels, the slabs in said core being staggered with respect to the panels in said inner and outer sheets so

that the joints in said core are arranged in non-coinciding relationship with respect to the joints in said inner and outer sheets through the thickness of said wall section.

8. The method of making a heat-insulating wall section, comprising fabricating a pair of outer sheets each formed essentially of plywood, each of said outer sheets including a plurality of individual panels cemented together in abutting edge relationship and a plurality of elongated ribbon-like metal splines arranged mutually in aligned grooves respectively provided in the abutting joined edges of said panels, providing a plurality of individual block-like slabs each formed essentially of foamed polystyrene, producing a sandwich structure of said outer sheets and a number of said slabs arranged as a composite core therebetween, wherein said slabs in said core are arranged in abutting edge relationship with each other and with moisture-impervious adhesive layers respectively disposed between the abutting joined edges of said slabs and with moisture-impersions adhesive layers respectively disposed between the faces of said core and the adjacent inner surfaces of said outer sheets, and then subjecting said sandwich structure to pressure by passing the same through a pair of co-operating pressure rollers.

9. The method according to claim 8, whereins aid sandwich structure is subjected to a pressure in the range 25 to 50 pounds per square inch in the passage thereof between said pair of co-operating pressure rolls.

10. The method of making a heat-insulating wall section, comprising fabricating a pair of outer sheets each formed essentially of plywood, each of said outer sheets inlcuding a plurality of individual panels cemented together in abutting edge relationship and a plurality of elongated ribbon-like metal splines arranged mutually in aligned grooves respectively provided in the abutting joined edges of said panels, providing a plurality of individual block-like slabs each formed essentially of foamed polystyrene, applying a first moisture-impervious adhesive coating to the inner surface of one of said outer sheets, placing a number of said slabs upon said first coating in abutting edge relationship with each other and with moisture-impervious adhesive layers respectively disposed between the abutting joined edges of said slabs so as to produce a composite core, applying a second moisture-impervious adhesive coating to the inner surface of the other of said outer sheets, placing the other of said outer sheets upon said core with said second coating in contact therewith so as to produce a composite sandwich structure, and then subjecting said sandwich structure to pressure by passing the same through a pair of co-operating pressure rolls.

11. A prefabricated heat-insulating wall section constructed substantially as herein described with reference to the accompanying drawings.

12. The method of making a heat-insulating wall section substantially as herein described with reference to the accompanying drawings.

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Dated this 28th day of December 1960.

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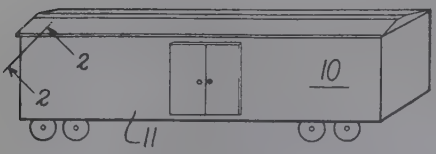
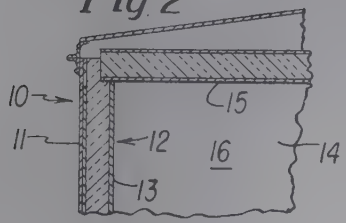


Fig. 1

Fig. 2



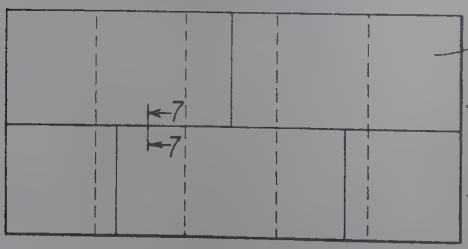


Fig. 3

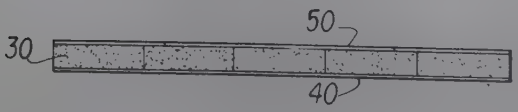


Fig. 4

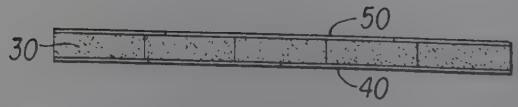


Fig. 5

of REMFRY & SON
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GENERAL AMERICAN TRASPORTATION CORPN. (2 Sheets) Sheet 2.
No. 74711.

Fig. 6

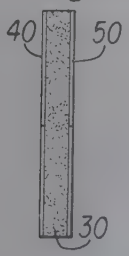


Fig. 7

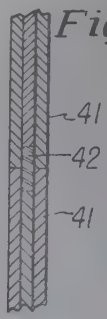


Fig. 8

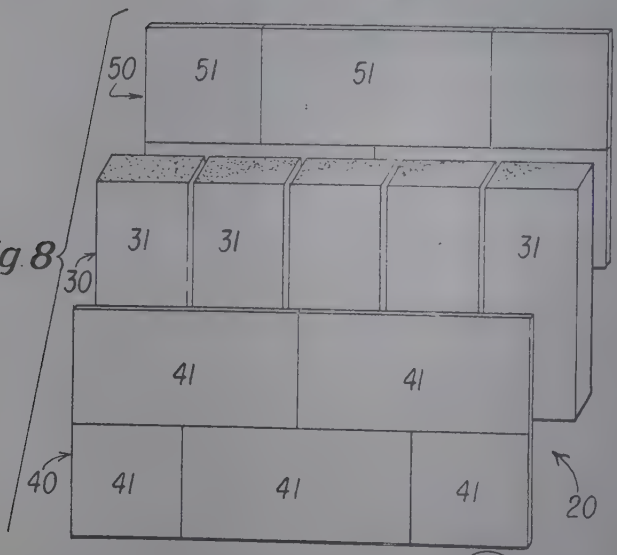
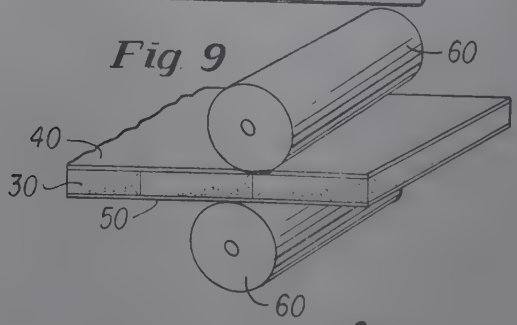


Fig. 9



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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74712, filed 28th December 1960. 7th Paus 1882 (SAKA). Reciprocity date (United Kingdom)— 31st December, 1959. (Accepted 28th June 1962.)

IMPROVEMENTS IN OR RELATING TO SECTION INSULATORS FOR USE IN OVERHEAD CONDUCTORS OF ELECTRIC TRACTION SYSTEMS.

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The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to section insulators of electric traction systems in which current is collected from an overhead contact wire by means of a collector of the kind comprising a shoe or bar which extends transversely of the contact wire and is, in its operative position, pressed upwards into contact with the underside of the contact wire, usually, but not in all cases, by mounting it on a spring loaded pantograph mechanism mounted on the roof of a vehicle.

For the purpose of sectionalising the overhead electric conductor system, or for other reasons, it is the practice to insert section insulators in the system. These must effectively electrically insulate from one another the sections between which they are inserted, transmit the tension in the conductor or conducors in which they are inserted, and, thirdly, serve to transfer the collector smoothly from the contact conductors in one section across the section insulator to the contact conductor in the next section. Such insulators as have hitherto been in general use have been of massive construction and unduly heavy. They have the disadvanage of forming in the contact wire a "hard" spot which gives rise to loss of contact and hence to severe arcing as the collector runs through, especially when it runs through at high speeds.

In the specification of our Co-pending Application No. 68579 we have described an improved form of section insulator through which a current collector can run at high speed without the occurence of an undue degree of arcing. In that improved section insulator the contact wires of the two neighbouring sections are mechanically connected together but electrically insulated from one another by a pair of ties which serves to transmit the tension and as runners to transfer the collector smoothly from the one contact wire to the other. Each of such ties comprises major and minor end parts of metal united by an intervening tension insulator of resin bonded glass fibre rod or tube. The ties are attached at their ends to the ends of the two contact wires and are so disposed that the major metal end part of the one lies at the opposite end of the section insulator to the major metal end part of the other, their respective lengths being such that the one overlaps the other. Central parts of the ties are held in spaced horizontal relationship, one lying on one side of the longitudinal centre line of the insulator and the other on the other side by means which may serve as a point of attachment to a support. Beyond each end of their central parts the runners gradually converge as they approach an end fitting to which they and the neighbouring end of the contact wire are secured and then continue alongside and in close proximity to that contact wire, the two runners together forming an elongated structure of approximately hexagonal form. Section insulators of this kind will hereinafter be referred to as "section insulators of the kind described."

The term "resin bonded glass fibre rod or tube" is used in this specification and in the claims which form part thereof to mean a rod or tube of thermosetting or cold setting synthetic resins of a kind which sets to a hard and infusible and generally insoluble condition, with or without heat, reinforced with glass or other inorganic high tensile strength filaments (hereinafter referred to as "glass filaments") which are distributed through the mass of the body and which, in the case of a rod, lie substantially parallel to one another throughout the length of the rod and preferably substantially all of which are of the same or approximately the same length as the rod. In the case of tubes, it is preferable for some at least of the glass filaments to extend circumferentially or helically of the tube. Rods of resin bonded glass fibre may be manufactured by coating a group of continuous glass filaments, disposed substantially parallel to one another, with a polyester resin by immersion in the resin in a liquid or semi-liquid reactive condition, then drawing the filaments through a die of diameter slightly greater than that of the rod required and curing the resin. The resin may be allowed to harden at room temperature or be baked to cause the resin to set, in accordance with the type of resin used. The curing may commence as the rod passes through the die. Tubes of resin bonded glass fibre may be manufactured by wrapping or helically lapping, or by both helically lapping and longitudinally applying glass fibre rovings or tapes of woven glass fibre, impregnated with the resin in a liquid or semi-liquid reactive condition, on mandrels, allowing or causing the resin to set, and withdrawing the mandrels.

In the aforesaid prior specification it is stated that where the section insulator is intended to operate in traction systems of which the voltage is sufficiently high to produce carbon tracking on the resin bonded glass fibre insulator, we prefer to protect the insulator by means of a coating or sleeve of an insulating material that is resistant to tracking, for example, polytetrafluoroethylene (hereinafter termed P.T.F.E.) and polytrifluorochloroethylene (hereinafter termed P.T.F. C.E.).

We have now found that section insulators of the kind described have a shorter life than is economically desirable when used in situations where collectors pass through the insulators at high speeds as the P.T.F.E. covered glass fibre runners are not sufficiently resistant to the abrasive action of the carbon or copper collectors.

By the present invention we provide an improved form of section insulator of the kind described which will better withstand the abrading action of an impact imparted by a current collector traversing the section insulator at high speeds, by which is meant speeds in the range of 80 to 100 or more miles per hour.

In our improved form of section insulator we provide in parallel with each resin bonded glass fibre insulator, at least one auxiliary insulating runner of wear-resistant insulating material. The under surface of this auxiliary runner will lie in the same plane as or slightly below that of the neighbouring resin bonded glass fibre insulator. At each end, the running face of this auxiliary runner or of its supports may gradually rise towards the level of the neighbouring running surfaces of the section insulator.

The auxiliary runner may have the form of a rod of circular or rectangular cross-section or it may be of channel section and be mounted so that the side walls of the channel are dependent, one on each side of the tension insulator. Where a runner of circular or rectangular cross-section is used we prefer to use a single runner on the inner side of each tension insulator. Alternatively, we may use a pair of auxiliary runners with each tension insulator, one runner on each side of the tension insulator.

The auxiliary runners are preferably of ceramic material, it being understood that the word "ceramic" when used herein embraces materials produced by the firing of plastic raw materials glass and fused silica. Of the ceramic materials we prefer those having a high alumina content and toughened glass By "toughened glass" we mean glass which has been treated to provide it with a skin which is in a permanent state

of compression and a core which is in a permanent state of tension.

We prefer to use toughened glass runners of rectangular cross-section and to position these one on the inner side of each resin bonded glass fibre insulator runner, with one edge, the lower edge, lying in the same plane as the lower or running surface of the insulator runner. Where the under surface of each toughened glass runner lies slightly below that of the neighbouring resin bonded glass fibre insulator each end of each toughened glass runner may be ground or otherwise shaped to curve gradually upwards away from such plane.

Each auxiliary runner extends endways beyond each end of the neighbouring tension insulator runner and is preferably secured at its ends to the supports of the neighbouring tension insulator. In order to accommodate any differences in thermal or mechanical expansion that may occur between the wear-resistant material of the auxiliary runner and the resin bonded glass fibre of the tension insulator, we prefer to secure the ends of the auxiliary runner to the supports of the neighbouring tension insulator by means which together permit expansion or contraction of the auxiliary runner relative to, and in a direction parallel with, the tension insulator. Each auxiliary runner may be pivotally secured to the neighbouring tension insulator supports to prevent the imposing of bending stresses in the auxiliary runner due to flexing of the contact wires and the ties of the section insulator.

Toughened glass rod of circular cross-section having one end curved are obtainable and may be used in pairs as auxiliary runners, the curved ends being disposed at opposite ends of the tension insulator runner and the straight parts of the rods being mounted inclined at a small angle to one another so that the collector is transferred to the other runner of a pair before it reaches the straight end of the runner it first engages.

Although in the description of the invention and in the statement of claim the term "auxiliary runner" has been used as a matter of convenience, it will be understood that in cases where the under surface of an auxiliary runner lies below the level of the running surface of the neighbouring resin bonded glass fibre insulator to such an extent that the under surface of the auxiliary runner only is in contact with the current collector, the so-called "auxiliary runner" will, in effect, be a main and possibly the only insulating runner in contact with the current collector on that side of the section insulator.

In this specification the term "horizontal" is employed to indicate a line on a plane that is parallel to the running track beneath.

An example of our preferred form of section insulator constructed in accordance with the invention will now be described with reference to the accompanying drawings in which:

Figure 1 is a diagrammatic plan view of the section insulator;

Figure 2 is a half plan view of the section insulator diagrammatically shown in Figure 1, the section insulator being symmetrical about its transverse centre line;

Figure 3 is a side elevation of the part of the section insulator shown in Figure 2;

Figure 4 is a side elevation of an anchorage fitting used in the section insulator;

Figure 5 is an end elevation of the anchorage fitting shown in Figure 4;

Figure 6 is a side elevation of a cylindrical bar used in combination with the anchorage fitting for clamping the runners to the end of the contact wires;

Figure 7 is an end elevation of a contact wire clamp used to clamp the end of each runner to the contact wire;

Figure 8 is a plan view of the malleable metal compression fitting used in securing one end of a tension insulator to the neighbouring metal runner;

Figure 9 is a side elevation of the fitting shown in Figure 8;

Figure 10 is a view partly in section and partly in elevation of the method used for attaching a composite tension insulator to the malleable metal compression fitting shown in Figures 8 and 9;

Figure 11 is a plan view of a tension insulator of the section insulator with an auxiliary runner mounted alongside;

Figure 12 is a partly fragmental side elevation of the view shown in Figure 11;

Figure 13 is a section taken on the line XIII-XIII in Figure 11,

Figure 14 is a section taken on the line XIV-XIV in Figure 11;

Figure 15 is a plan view of an auxiliary runner;

Figure 16 is a side elevation of the auxiliary runner shown in Figure 15;

Figure 17 is a plan view of an auxiliary runner support, and Figure 18 is a side elevation of the auxiliary runner support shown in Figure 17.

In the preferred form of section insulator shown in Figures 1 to 3 the contact wires 1 of two neighbouring sections are mechanically connected together by electrically insulated from one another by a pair of tensioned runners 2, each of which comprises a major metal end part 4 each of inverted 'T' section with the head of the 'T' convexly curved transversely to its length to form the running surface of the runner, united by a composite tension insulator 5 comprising a resin bonded glass fibre rod of circular cross-section surrounded by a P.T.F.E. sleeve. The runners 2 extend parallel to each other over the central part of their length and are spaced apart, one lying on one side of the longitudinal centre line of the section insulator and the other on the other side. The major metal end part 3 of one of the runners 2 lies at the opposite end of the section insulator to the major metal end part 3 of the other runner, their respective lentghs being such that one overlaps the other. Beyond each end of its central part each runner 2 gradually converges towards the other as it approaches an anchorage fitting 6, to which it and the end of the neighbouring contact wire 1 are secured, and then continues alongside and in close proximity to the contact wire to a contact wire clamp 7 that clamps the end of each runner to the contact wire at that point.

In parallel with each tension insulator 5 serving as part of a runner 2 is an auxiliary runner 8 which extends along the inner side of, and is geometrically parallel with, the tension insulator and which comprises a rectangular section bar of toughened glass disposed with its major surface normal to the horizontal and its lower edge flush with the lower surfaces of the P.T.F.E. covered resin bonded glass fibre tension insulator. The auxiliary runner 8 extends at both ends beyond the ends of the tension insulator 5 and is held by clamping means 9 which is also secured to metal sleeves compression jointed to the ends of the glass fibre rod. Attached to the clamping means 9 at each end of the tension insulator 5 is a pair of arcing horns 10, one of which is on the outer side of the tension insulator and the other of which is on the inner side of the auxiliary runner 8.

Between their ends the runners 2 are held in spaced horizontal relationship by braces 12 which brace the major metal end part 3 of each runner to the neighbouring minor metal end part 4 of the other runner. The ends of the braces 12 have feet 13 which are set at an appropriate angle for riveting to the central stiffening web 14 of each runner 2, the angle corresponding to the angle of convergence of the runner at the bracing point.

In the neighbourhood of the anchorage fitting 6 and beyond where the runners 2 lie alongside the contact wires 1 the part of the running surface lying on the inside of the web 14, i.e., between the web and the longitudinal centre line of the section insulator, is removed to allow the web 14 to be bolted against the adjoining side wall of the anchorage fitting 6 and the runner to lie alongside the contact wire. In the region of the anchorage fitting 6 the part of the running surface of each runner 2 lying on the outside of the web 14 is also removed to provide accommodation for the nuts securing the web to the fittings. Also part of the running surface on each side of the web 14 is removed at the extremities of each runner 2 to facilitate clamping it to the contact wire 1 by the contact wire clamp.

7. At these extremities the lower edge 15 of the running surface is cut away to provide an upwardly curving end to each running face of each runner.

Each contact wire 1 is secured at its end to each of the converging runners 2 by the anchorage fitting 6. This fitting is shown in Figures 4 and 5. It is formed with an undercut groove 17 in its lower edge which is designed to receive the upper part of the standard profiled contact wire. The wire is held in the groove by a pair of pinch screws 18 (Figures 2 and 3) set at an angle of 60° to the wire to exert on the wire a thrust having a component opposed to the pull on the wire. The end of the fitting 6 nearer the end of the contact wire is enlarged to form a block 19 having a pair of parallel flat side walls which project downwards to form a pair of flat horizontal faces 20 level with the running face of the anchored end of the contact wire. In the block 19 are a pair of circular holes 21 extending from one side to the other, the axes of which are tangential to the top of the groove 17 for the contact wire. A cylindrical bar 22 is a push fit in each of the holes 21. The bar 22, which is shown in Figure 6, has a substantially semi-circular transverse slot 23 to allow passage of the contact wire. Projecting from each end face of each bar 22 is a cylindrical stud 24 screw-threaded at its outer end. Each runner 2 is drilled at appropriate points in its length to receive two of the studs 24 so that it can be clamped beween a side wall of the block 19 and a protection plate 25 by nuts 26 on the studs. To provide a smooth run-through for a current collector approaching the section insulator in a tilted position, the bottom face of each protection plate 25 is flanged and shaped to match the profile of the running surface of the runner 2 which as previously desrbed, has been cut away in the region of the fitting 6. The studs 24 are so located that the runners 2 are anchored to the contact wires 1 through the fittings 6 with their running surface level with the running surface of the contact wires. In the upper part of the block 19 is an eye 27 for the attachment of a loop dropper (not shown) that serves to suspend the fitting from the catenary wire above it. Additional support for the section insulator is given by further loop droppers (not shown) which are attached to the braces 12. The block 19 is also provided with a horizontal socket 28 to receive an eye bolt and means for temporarily tying the two contact wire anchoring devices to one another before cutting the contact wire 1 and attaching the runners 2, or when renewing component parts of the section insulator during maintenance.

The neighbouring ends of each of the runners 2 are clamped to the contact wire 1 by a contact wire clamp 7. As will be seen from Figure 7, the clamp 7 is constructed of two identical parts 30 each of which has its inner side face so shaped that when the two parts are placed in position with their inner side faces abutting a groove 31, designed to receive the upper part of the standard profiled contact wire, is formed in the lower edge of the clamp. A circular hole 32 extends through both parts 30 from one side of the clamp 7 to the other, the axis of which is tangential to the top of the contact wire held in the groove 31. A cylindrical bar, which is similar in design to the bar 22 already described with reference to Figure 6, is a push fit in the hole 32. Each runner 2 is drilled at an appropriate point in its length to receive the projecting stud of the bar so that the runner can be clamped to a side wall of the clamp 7 by nuts 34 on the studs. As in the case of the anchorage fitting 6, the location of the studs on the bar is such that the runners 2 are anchored to the contact wires 1 through the clamp 7 with their running surface level with those of the contact wires.

Each end of each tension insulator 5 is attached to the neighbouring end of the associated metal end part of the runner 2 by a malleable metal clevis compression fitting 37, shown in Figures 8 and 9, having at one end a sleeve 38, with a stepped bore 40, which is compression jointed to the end of the tension insulator and having at its other end a clevis 39 for receiving the end of the web 14 of the inverted 'T' section metal part of the runner. At the end of the sleeve 38 is formed a rectangular block 41 in the upper part of which is a tappd hole 42 to receive a bolt for securing an auxiliary runner support to the fitting 37 as will be described hereinafter. As is more clearly shown in Figure 10, the end of the P.T.F.E. sheath 44 which surrounds the resin bonded glass fibre rod 45 forming the tension insulator 5 is cut back to expose a length of the rod and the cut-back end of the sheath is stepped. The stepped bore 40 of the sleeve 38 of the malleable metal fitting 37 fits the resin bonded glass fibre rod 45 and also the locally reduced end of the P.T.F.E. sheath 44. When the sleeve 38 is compressed on to the bare end of the rod 45 and on to the reduced end of the sheath 44, the underside of the sleeve forms a smooth continuation of the sheathed rod. The lower edges of the clevis end 39 of the fitting 37 also form a smooth continuation of the sleeve 38 and are level with the running face of the metal part of the runner 2. In this way each runner 2 comprising a major metal end part 3 and a minor metal end part 4 separated by a tension insulator 5 presents throughout its entire length a smooth and subtantially level surface for guiding a collector across the section insulator without any substantial deliberate deflection from its nominally level path.

On referring to Figures 11 to 14, it will be seen that the tension insulator 5 is connected at each of its end to the neighbouring metal end part of the runner 2 by the malleable metal fitting 37. Alongside the inner side of, and in parallel with, the tension insulator 5 is mounted an auxiliary runner 8 which runs geometrically parallel with, and extends beyond the ends of, the tension insulator. The auxiliary runner 8, as shown more clearly in Figures 15 and 16, comprises a rectangular section bar 50 of toughened glass having each of its ends of reduced cross-section. Each end of the bar 50 is secured in an end casting 51 of rectangular section by Roses metal 52 which, when the auxiliary runner 8 is assembled, is applied by pouring the metal through two holes 53 in the top of the casting. The casting 51 is provided at its end face with a projecting lug 54 in which is a horizontal slot 55 which is open at its outer end.

The pair of arcing horns 10 of rectangular section mounted one on the outer side of the tension insulator 5 and the other on the inner side of the auxiliary runner 8 running alongside thereof are secured at their outer ends to the runner 2 by means of duplex spring hollow dowel pins 62, which also serve to clamp the webs 14 of the runners 2 to the clevis end 39 of the malleable metal fitting 37. Each of the arcing horns 10 has a vertical plate 63 riveted to its inner side face and a vertical slot 64 is provided in the upper part of each plate.

Mounted above each of the malleable metal fittings 37 is an auxiliary runner support 77 which is shown in Figures 17 and 18 and which comprises a metal casting 78 of approximately 'T' section over the greater part of its length. One end of the web of the 'T' is slightly enlarged and is provided with a hole 79 whose axis is horizontal. A boss 80 is formed at the other end of the support 77 through which passes a vertical hole 81. Adjacent the boss 80 a cylindrical block 82 is formed in which is a hole 83 having its axis parallel with, and in the same horizontal plane as, that of the hole 79. On the upper part of the block 82 is formed a rectangular boss 84 through which passes a tapped hole 85 whose axis is vertical.

One auxiliary runner support 77 is mounted above each of the malleable metal fittings 37 so that its horizontal hole 83 is aligned with the vertical slots 64 through the pates 63 rivetted to the arcing horns 10. A bolt 86 passing through the vertical hole 81 screws into the vertical hole 42 in the end of the fitting 37 and clamps the support to the fitting. The outer end of the auxiliary runner support 77 is secured by a bolt 87 between a pair of clamping jaws 88 which clamp the outer extremities of the arcing horns 10 to the web 14 of the runner 2.

As previously described the auxiliary runner 8 is disposed alongside the tension insulator 5 with its major surfaces normal to the horizontal and it lower

of member 22, determines a given cross-section area for throttled passage 21.

In the angular position of member 22 which corresponds to the minimum cross-section of the throttlend passage, that is to say in the position shown by Fig. 1, said member 22 connects the portion of conduit 20 located upstream of the throttled passage with a discharge conduit 26, through a groove 25 provided in the side wall of member 22. Advantageously, the cross-section of said groove 25 is chosen in such manner that, for very low loads of the engine (for instance when it is being started), shuttle 7 is not lifted from its abutment 18, so that the whole of the liquid coming from conduit 11 is evacuated to the outside through groove 25 and conduit 26, which ensures an increase of the rate of delivery of the pump when the engine is being started. On the contrary, when the engine is idling or when its speed is higher, the cross-section of groove 25 is not sufficient to enable the liquid coming from conduit 11 to be evacuated through said groove and the shuttle works normally, that is to say in the following manner.

During every delivery stroke of piston unit 2, 8, shuttle 7 is moved upwardly until it reaches the position where it clears conduit 19, in which position it opens discharge conduit 6, which causes injection to be stopped. As long as the speed of the engine and consequently that of the pump are lower than a given value, the shuttle, between two consecutive delivery strokes of piston unit 2, 8, comes back into its position of rest against abutment 18. The stroke of the shuttle therefore corresponds to the axial distance between this abutment and the orifice of conduit 19. As soon as the speed of the piston unit 2, 8 exceeds this given value, the shuttle, the return strokes of which are braked by throttled passage 21, can no longer return, between two consecutive delivery strokes of said piston unit, into its position of rest, that is to say into the position where it is applied against abutment 18, but it is stopped before it can reach this position by the liduid delivered by auxiliary piston 8 and which constitutes a "liquid abutment" which is thus substituted for the mechanical abutment 18. The return strokes of the shuttle are therefore shortened and said shuttle opens discharge conduit 6 at an earlier time during every delivery stroke of piston 2 as the speed increases more and more above said predetermined value, which produces a corresponding reduction of the amount of fuel injected for every stroke of the pump piston.

The liquid abutment effect consists essencially in preventing the engine from exceeding a given speed. However, it is often necessary to vary the maximum output per cycle of the pump, that is to say the amount of fuel that determines the torque of the engine, this variation being obtained for instance as a function of the speed or of another factor of operation of the engine.

In order to permit such a correction of the engine torque, I make use, according to the essential feature of the present invention, of means for varying the distance existing between solid abutment 18 and the orifice through which discharge conduit 19 opens from cylinder 13. For this purpose, it might be possible to vary the position of the orifice of said conduit 19 in cylinder 13. However it seems simpler and more advantageous to displace abutment 18. For instance, in the embodiment shown by the drawings (Figs. 1 and 2), rod 18 which constitutes said abutment is slidable under the effot of a cam 27 itself movable in a cylinder 28 against the action of a spring 29 and under the action of a dydraulic pressure. This pressure depends advantageouly upon the speed of the engine on which the injection pump is mounted.

Concerning cam 27, in the embodiment shown by Figs. 1 and 2 it is given the shape of a frustum of a cone the generatrix of which has a shape corresponding to the desired correction of the torque, which correction must be of course adapted to every type of engine or to every way of operating an engine of a given type. This frustum of a cone may be provided between two cylindrical portions 30, 31 which act as pistons and are slidable in the above mentioned cylinder 28, portion 30 being subjected to the variable hydraulic pressure, whereas portion 31 is subjected to the action of spring 29.

The means for producing a variable hydraulic pressure in the chamber of cylinder 28 that cooperates with piston 30 are made as follows:

A volumetric pump 32 (i.e. a pump which delivers an amount of liquid per unit of time proportional to the speed at which it is operated) is driven at a speed proportional to that of the engine, this pump 32 being for instance a gear pump. This pump may also be at the same time the pump to which are connected the feed conduits 3 and 10 of cylinders 1 and 9 respectively. This pump 32 delivers a liquid, which is preferably the fuel itself, into a delivery conduit 33 from which are branching off, on the one hand a conduit 34 which leads to said working chamber of cylinder 28 and on the other hand an outlet 35. A conduit 36 connects tank 37 to the inlet of pump 32. It will be understood that the pressure in conduits 33 and 34 varies in accordance with the speed of pump 32 and therefore in accordance with the speed of the engine. Preferably, outlet 35 is not of constant cross section but it has a cross-section which also varies in accordance with the pressure in conduit 33 and therefore in accordance with the speed of the engine, this variation being preferably such that the cross-section of the outlet increases when the speed increases and decreases when the speed decreases. For this purpose, I provide a slide valve 38 which determines the cross-section of the outlet orifice and which is placed, on the one hand under the action of the pressure existing in conduit 33, and on the other hand under the action of an opposing spring 39, a groove 40 provided in slide valve 38 being arranged in such manner that it opens outlet orifice 35 more and more as the pressure 33 increases.

In the embodiment illustrated by Figs. 1 and 2, the correction produces a displacement of abutment 18 such that the stroke of the shuttle becomes shorter and shorter as the speed increases, which produces a reduction of the maximum amount of fuel injected per cycle of operation of the pump and consequently a reduction of the engine torque when the speed increases. Of course I might, with similiar means, obtain a displacement of abutment 18 in the opposed direction, that is to say in a direction producing a lengthening of the shuttle stroke, and therefore an increase of the engine torque when the speed increases.

In the embodiment of the invention illustrated by Figs. 3 and 4, solid abutment 18 is carried by a screw-threaded element 127 the screw-threads of which are such that a pressure exerted on rod 18 cannot cause this rod to rotate. Preferably, as shown, element 127 and abutment 18 are integral with each other.

The axial position of solid abutment 18 can be modified by rotating element 127 which is screwed in the end of cylinder 13.

In order to rotate element 127 there is provided, at the end thereof opposed to solid abutment 18, a disc 127*a* which carries, eccentrically positioned thereon, a finer 127*b* which, through a sliding member 127*c*, co-operates with a transverse slot 130*a* provided in a piston 130 slidable in a cylinder 128 having its axis at right angles to the axis of element 127. It will be understood that the angular position of threaded element 127 and therefore the axial position of abutment 18 depend upon the position of piston 130 in its cylinder 128. Of course, the depth of slot 130*a* and the height of sliding member 127*c* must be sufficient to enable finger 127*b*, whatever be the axial position of abutment 18 and of threaded element 127, to be always in engagement with said sliding member.

The position of piston 130 depends upon the speed of operation of the pump and therefore upon the speed of the engine on which said pump is mounted to feed fuel thereto. For this purpose, piston 130 is subjected to a pressure variable with this speed, this pressure acting upon said piston against the action of a return spring 129.

The means for producing this variable pressure are, in the case of Figs. 3 and 4, the same as those shown with respect to Fig. 2.

The effect of an axial displacement of abutment 18 under the action of a rotation of threaded element 127, is the same as that obtained by a longitudinal displacement of conical cam 27. However control of abutment 18 through the means illustraded by Figs. 3 and 4 has a higher sensitiveness and follows with a greater accuracy the variations of pressure in cylinder 128.

This is due to the fact that the shocks exerted by shuttle 7 upon abutment 18, at the end of the return stroke of said shuttle, are supported by the frame of the pump in which threaded element 127 is screwed and are not transmitted to piston 130. The movement for controlling this piston in its cylinder 128 are therefore no longer subjected to any stress that might interfere with the balancing of the opposite forces acting upon said piston.

Fig. 5 shows a modification of the device controlling the rotation of threaded element 127.

According to this modification, finger 127*b* is engaged in a groove 130*b* of piston 130, this groove having a width substantially equal to the diameter of finger 127*b*, so that sliding element 127*c* of the construction of Figs. 3 and 4 has been dispensed with. Of course, the depth of groove 130*b* and the length of finger 127*b* must be determined in such manner that, whatever be the angular position of threaded element 127 and the axial position of abutment 18, finger 127*b* always remains engaged in groove 130*b*. The co-operation between piston 130 and threaded element 127 is of course the same as in the case of Figs. 3 and 4.

Rotation of the threaded element might also be obtained by a rack driven together with piston 130 and co-operating with a toothed wheel rigid with threaded element 127.

With the arrangement according to my invention, the engine torque may be adapted to every type of engine and, for every particular engine, to the use for which it is intended (automobile vehicles, electricity producing power plants and the like, agricultural tractors, etc).

Other modifications may be as follows :

— cam element 27 of Figs. 1 and 2 might have several faces having generatrices of different curvatures which would correspond, either to different types of engines, or to different ways of using a given type of engine, the cam being then adapted to be moved, not only axially but also in rotation about its axis so as to bring the different faces into active position where they co-operate with abutment 18 ;

— the hydraulic pressure, variable with the speed of the engine, might, instead of acting upon a piston which controls cam 27 or threaded element 127, be transmitted to the inside of a deformable box the expansion of which would produce the displacement of said elements, so that perfect liquidtightness would be obtained in a very simple manner ;

— the translatory movement of the cam of Figs. 1 and 2 might be replaced by a rotary movement of this cam ;

— displacement of the abutment might be produced in response to variations of a factor of operation of the engine other than the speed thereof, for instance in accordance with the position of the throttle pedal thereof or of a handle for controlling said engine.

In a general manner, while I have, in the above description, disclosed what I deem to be practical and efficient embodiments of my invention, it should be well understood that I do not wish to be limited thereto as there might be changes made in the arrangement, disposition and form of the parts without departing from the principle of the present invention as comprehended within the scope of the accompanying claims.

I CLAIM :—

1. A self-regulating reciprocating pump for injection of fuel into internal cobustion engines wherein regulation is obtained by means of a movable member called "shuttle" adapted to be moved, under the opposed actions of a power liquid and of a spring, between a position of rest determined by a mechanical abutment and a final position determined by the opening, by the shuttle itself, of a discharge port through which said power liquid escapes, the return movement of the shuttle from this position toward the position of rest being braked by a throttled passage through which the shuttle must force the power liquid, characterized by means for varying the distance between the mechanical abutment which determines the position of rest of the shuttle and the discharge orifice the position of which determines the end of every outward stroke of the shuttle.

2. A pump according to claim 1 wherein variation of this distance is obtained by a Displacement of the mechanical abutment, whereas the position of the discharge orifice is fixed.

3. A pump according to claim 1 wherein variation of this distance takes place in response to a variation of a factor of operation of the engine which is fed with fuel from the pump.

4. A pump according to claims 1 and 2 wherein the displacement of the abutment is produced by a cam.

5. A pump according to claim 4 wherein the cam has the form of a cone the generatrix of which corresponds to the desired correction of the torque of the engine and which is movable longitudinally in a direction transverse to the direction along which the abutment is displaceable.

6. A pump according to claims 4 and 5 wherein the wall of the cam is provided with several faces having different generatrices, such a cam being movable not only axially but also by rotation about its axis.

7. A pump according to claims 1 and 2 wherein the abutment is supported by a screw-threaded element the threads of which are such that it cannot be caused to move by a thrust exerted axilly thereon and which can be rotated about its axis to modify the position of the abutment.

8. A pump according to claim 7 wherein the threaded element is rotated through mechanical means driven by a piston movable transversely to the axis of the threaded element.

9. A pump according to claims 1 to 3 wherein the means for producing the displacement of the abutment are actuated by the differential action of a hydraulic pressure variable with the speed of the engine and of the force exerted by an opposing spring.

10. A pump according to claim 9 wherein the hydraulic pressure is produced by a hydraulic regulating device comprising a volumetric pump driven at a speed proportional to the speed of the engine, and an outlet orifice in the delivery conduit of this volumetric pump for outflow of the liquid delivered by it, this outlet orifice having a cross-section which is variable in accordance with the speed of the engine so that said cross-section increases when the speed increases and decreases.

11. A self-regulating reciprocating pump for injection of fuel into internal combustion engines substantially as hereinbefore described with reference to and as shown in the accompanying drawings.

R. HALL
of REMFRY & SON.
Agent for the Applicants.

Dated this 28th day of December 1960.

Printed by The Nelys Printing Works, Calcutta-1.

P. E. BESSIERE.
NO. 74713 of 1960.

(2 Sheets)

Sheet 1.

Fig. 2.

Fig. 1.

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P. E. BESSIERE. No. 74713 of 1960. (2 Sheets) Sheet 2.

Fig.3.

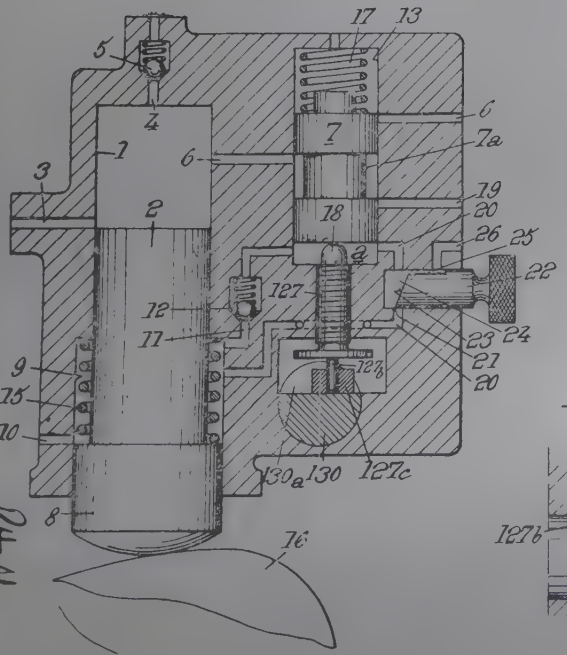


Fig.4.

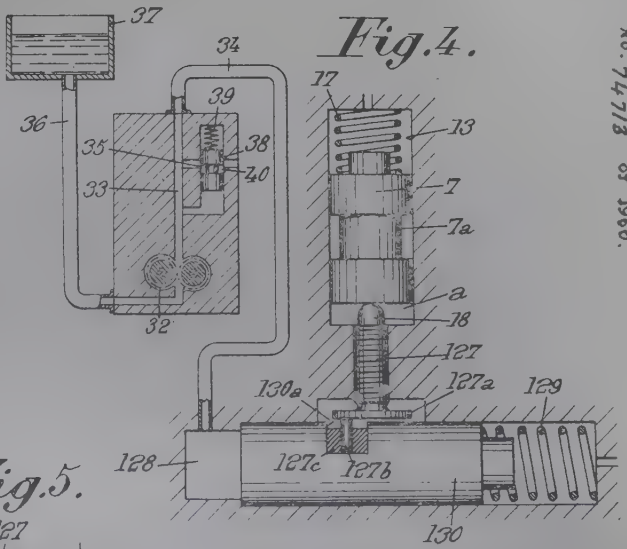
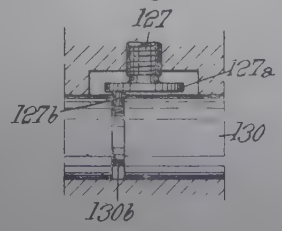


Fig.5.



Agent for the Applicant

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74715, filed 28th December 1960. 1st Puas 1882 (Saka). (Accepted 9th May 1962.)

IMPROVED PROCESS FOR TREATMENT OF MATERIAL, PARTICULARLY TREATMENT OF METALS TO RETARD CORROSION

ROBERT HALL, A BRITISH SUBJECT, OF STEPHEN HOUSE, DALHOUSIE SQUARE, CALCUTTA, WEST BENGAL, INDIA.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to a process for treating metals to retard corrosion, and more particularly, to a novel process for treating material having a zinc surface to inhibit white rusting and generally improve corrosion resistance. The invention further relates to the novel corrosion inhibited product produced by the process described herein.

The invention will be described and illustrated hereinafter with specific reference to a process for inhibiting "white rust" formation on materials having a zinc surface. However, it will be recognized by those skilled in the art that the process of the present invention also may be useful in retarding or inhibiting other types of corrosion and generally improving corrosion resistance. The term "zinc surface" as used in the specification and claims is intended to include a surface of a material subject to white rusting which is composed of zinc or predominantly of zinc. Examples of materials having a zinc surface subject to white rusting and suitable for treatment in accordance with the present invention include metallic forms or articles composed of zinc or predominantly of zinc, base metals such as ferrous metals or articles fabricated therefrom which are provided with a protective coating of zinc or zinc alloys containing a predominant amount of zinc, etc. It is understood that a suitable material for treatment may have a zinc surface as herein defined on only a portion of its surface area, and that such materials may be treated in accordance with the invention for the purpose of improving corrosion resistance of at least that portion of the surface area provided with the zinc surface.

A fresh, bright, untreated zinc surfaced material exposed to the atmosphere soon develops a surface film composed of corrosion products which are produced by the action of atmospheric substances, such as carbon dioxide, oxygen and moisture. As corrosion proceeds, the surface film tends to increase somewhat in thickness and the layer of corrosion products becomes a white deposit which renders the appearance of the zinc surface less pleasing to the eye. However, a zinc surfaced material directly exposed to weather is generally capable of giving long service without great loss of its appearance value since thin films of the corrosion products are more or less continuously removed by the elements, thereby preventing an appreciable build-up in the thickness of the layer of deposited corrosion products and leaving the zinc surface more or less uniform in appearance.

"White rust" is a term commonly used in the art to refer to a specific form of the above mentioned type of corrosion. It is generally considered to be a relatively thick white deopsit of corrosion products composed largely of zinc hydroxide and basic zinc carbonate which forms on unprotected zinc surfaced materials exposed to air and excessive amounts of moisture of water. The development of white rust occurs most rapidly when water is confined against the zinc surface by an overlying member, and it is particularly severe where fresh, bright, untreated zinc surfaced sheets or shapes are arranged during storage or shipment in such a way that water can accumulate between adjacent surfaces and remain for extended periods of time. For example, galvanized sheets useful in thee construction of metallic buildings are commonly stacked in open railway cars, either packaged or without packaging, and shipped over long distances, or stored for long periods of time awaiting shipment or use. Water accumulates between adjacent sheets during such periods due to sweating and white rust quickly forms on those portions of the sheets directly exposed to the water. Over a period of time. The coating of white rust gradually thickens and eventually the appearance of the originally bright, spangled galvanized surface is completely destroyed and it takes on the appearance of an inferior product.

The art has long sought a suitable process for treating zinc surfaced materials to effectively inhibit white rust formation. In general, the prior art processes involve the application of either a relatively thick protective coating such as oils, waxes, greases, varnishes, paints, etc., or various chemical treatments which deposit a thin protective coating integral with the zinc surface. In every instance, the prior art processes are unsatisfactory due, for example, to their being ineffective in substantially completely eliminating white rust formation for a reasonable period of time, too expensive, too time consuming for use in high-speed continuous galvanizing operations or the treatment results in a protective coating which must be removed prior to use of the treated zinc surfaced material. Also, in some instances, the coating substance either destroys or mars the appearance of the originally bright pleasing finish of the fresh zinc surface. The prior art chemical treatments, in particular, require careful control of operating conditions such as concentration of ingredients and temperature of treatment, and often exhibit a pronounced tendency toward formation of undesirable colored films on the treated zinc surface.

It is an object of the present invention to provide an improved process for inhibiting corrosion of zinc surfaced materials which overcomes the above mentioned diradvantages of the prior art processes.

It is still a further object of the present invention to provide an improved process for producing a corrosion inhibiting film on materials having a zinc surface by intimately contacting a hot zinc surface with effective amounts of a solution in a volatile solvent of at least one suitable substance which is a source of zinc ion and at least one suitable substance which is a source of chromate ion.

It is still a further object of the present invention to provide material having a zinc surface which is treated in accordance with the process of the present invention wherein the treated zinc surface is effectively inhibited against the formation of white rust and is not discolored or changed substantially in appearance.

Accordingly, the present invention provides a process for treating material having a zinc surface to improve corrosion resistance comprising intimately contacting a solution comprising at least one compound which is a source of zinc ion and at least one compound which is a source of chromate ion dissolved in a volatile solvent with the zinc surface of the material, the solution containing a ratio of zinc ion to chromate ion of 9 : 1 to 1 :9.5, the zinc surface being initially at a temperature above the boiling point of the solvent and below the melting point of zinc, the volume of solution contacted with the zinc surface being controlled and the temperature of the zinc surface being sufficiently elevated so as to volatilize the volatile components of the solution immediately after contact and produce an essentially colorless corrosion resistant film on the zinc surface.

Still other objects of the present invention and the advantages thereof will be apparent to those skilled in the art by reference to the following detailed description and the accompanying drawing, which graphically illustrates the white rust inhibiting value of atomized aqueous solutions of zinc chloride and chromic acid.

Price : TWO RUPEES.

In accordance with the present invention, materials having a zinc surface are treated for the purpose of depositing a corrosion resistant film on the zinc surface and thus improving corrosion resistance by intimately contacting zinc surface with a solution in a volatile solvent of at least one suitable substance which is a source of zinc ion and at least one suitable substance which is a source of chromate ion under conditions to be fully described hereinafter.

It is essential that the inhibitor solution be intimately contacted with the zinc surface, and that the zinc surface to be contacted with the solution be initially at an elevated temperature substantially above the boiling point of the particular volatile solvent used and below the melting point of zinc. For example, when water is the solvent, the initial temperature of the zinc surface to be contacted with solution should be from about 225°F. to about 600°F. In addition, the initial temperature of the zinc surface to be contacted with solution must be sufficiently hot so as to volatilize the volatile components present in the volume of solution which is intimately contacted with the surface substantially immediately after the instant of contact and to deposit a corrosion inhibiting film. When water is the solvent, an initial temperature below about 225°F. is not sufficiently elevated to accomplish the foregoing and to give generally satisfactory results; while at an initial temperature above about 600°F., the rate of evaporation is generally such as to prevent or to not allow sufficient time for intimate contact between the solution and the zinc surface before complete volatilization of the volatile components. Thus, in most instances, a proper degree of inhibition of white resulting is not imparted of the zinc surface under such conditions. Generally, better results are obtained when water is the solvent at an initial surface temperature between 250°F. and 350°F.

The inhibitor solution must be in intimate contact with the zinc surface before evaporation of the volatile components of the solution is complete. While the volatile components of the inhibitor solution are volatilized almost immediately after the solution is intimately contacted with the hot zinc surface, nevertheless a short period of time expires between the instant the solution is intimately contacted with the surface and complete volatilization of the volatile components, and this short period of time is necessary in order to achieve acceptable results. Thus, when operating at relatively high temperatures, steps must be taken to assure that at least a portion of the solution is being deposited in intimate contact with the zinc surface rather than the volatile components being volatilized completely while enroute from the source of spray to the zinc surface and thereby resulting in the surface being contacted with only dry particles of substances which were dissolved in the solution. In view of the foregoing, it may be advisable when operating at high temperatures to increase the volume of solution applied to a given surface area and decrease the concentration of the solution; or reduce the distance between the zinc surface and the atomizing device, i.e., reduce the distance of travel of the atomized solution; or increase the size of the individual droplets in the atomized spray, thereby decreasing their rate of evaporation; or lower the temperature of the air space through which the atomized spray travels while enroute from the spray source to the zinc surface, thereby decreasing the rate of evaporation.

The inhibitor solution of the present invention is a solution in a volatile solvent of a substance which is a suitable source of zinc ion and a substance which is a suitable source of chromate ion, and may be prepared by dissolving one or more compounds capable of providing at least one of such substances in the solvent. If either zinc ion or chromate ion is not present in the solution, then the degree of corrosion inhibition imparted to the treated zinc surface is not satisfactory. The ratio of zinc ion to chromate ion in the solution may vary over wide ranges. For example, by reference to the drawing, it may be seen that the treated corrosion inhibited product will exhibit a corrosion inhibition value of "Good" provided the ratio of zinc ion to chromate ion is about 9:1 to 1:9.5. It will also be noted that superior corrosion inhibition will be imparted to the product if the ratio of zinc ion to chromate ion is about 4:1 to 1:2. In most instances, for best results the inhibitor solution preferably should contain about equal concentrations of zinc ion and chromate ion.

The inhibitor solution may contain as solutes a suitable soluble zinc salt and a suitable soluble source of chromate ion. However, the anion of the zinc salt and the cation of the chromate preferably should be volatile under the conditions of the process of the invention. For example, when water is the volatile solvent, suitable zinc salts include zinc chloride and zinc nitrate and a suitable source of chromate ion is chromic acid.

In addition, the solution should be acidic but inasmuch as suitable solutes often provide a proper level of acidity, the presence of free mineral acid may not be necessary or desirable. For example, when chromic acid is the source of chromate ion, then the resulting acidic solution does not require the presence of free mineral acid. Since acidic solutions of chromate are generally considered to contain both chromate and dichromate, and perhaps other species of chromate, it may be necessary to make adjustments in concentrations where the concentration of "chromate" or "chromate ion" is referred to in the specification and claims. Where the concentration of chromate or chromate ion is referred to, it is understood to mean the gram ion concentration of CrO_4- which would be present in the solution if dichromate, or other species of chromate, were converted to CrO_4. Thus, a solution containing 1.0 gram ion of dichromate would be considered to contain 2.0 gram ions of chromate or chromate ion for the purposes of the present invention.

The degree of white rust inhibition imparted to the treated surface is largely determined by the amount of dissolved substances contacted with a given surface area and not, within reason, by the concentration of dissolved substances in the inhibitor solution. In general, contacting the surface with a relatively concentrated solution for a short period of time is equivalent to contacting the surface with a dilute solution for a larger period of time, provided equivalent amounts of dissolved substances are contacted with a given surface are in each instance. Thus, the concentration of zinc ion and chromate ion in the inhibitor solution may vary over wide ranges, it being understood that for the purpose of the specification and claims the zinc salt and source of chromate ion are considered to be completely ionized. Inasmuch as the solution is applied in such quantity as to be in intimate contact with the hot zinc surface for a very short period of time and is then volatilized substantially immediately, better results will be obtained at higher temperatures when the solution is relatively dilute, while at lower temperatures the solution may be more concentrated. When operating at a temperature of about 225° to 600°F., the concentration of zinc ion and chromate ion preferably should total about one gram ion. In addition, for preferred results, the volume of solution which is applied to each square foot of zinc surface treated should contain initially a total gram ion amount of about 4.3×10^{-5} to 3.5×10^{-4} mole of zinc ion and chromate ion. When such quantities of solution are applied to the hot zinc surface under the conditions taught herein, then adequate corrosion inhibition will result and a satisfactory corrosion inhibited product is produced.

When practicing the present invention, the zinc surface to be treated may be heated to the desired temperature and then intimately contacted with the atomized solution. The volatile components of the inhibitor solution are substantially instantaneously evaporated leaving behind a thin invisible colorless corrosion inhibiting film deposited on the zinc surface. The corrosion inhibited zinc surface does not require further treatment and generally further treatment such as a water wash is not preferred.

The solvent of the inhibitor solution may be a suitable volatile solvent in which the zinc salt and source of chromate ion are sufficiently soluble. In addition, the boiling point of the particular solvent selected should be such as to allow application of the solution to the hot zinc surface to be treated in accordance with the invention. Water is the most satisfactory solvent when the zinc salt is either zinc chloride or zinc nitrate and the source of chromate ion is chromic acid. However, alcohol, alcohol-water mixtures, or other suitable solvents will give

satisfactory results under proper conditions. When water is the solvent, water hardness is not detrimental to any great extent. Mildly hard water alters the inhibiting results only slightly, but somewhat better results generally will be obtained by the use of distilled water or deionized water and particularly where the water supply is extremely hard.

The zinc surface to be treated should be given a suitable conventional pretreatment for the removal of oils, greases, etc., where such are present. However, the presence of a thin film of oxide on the zinc surface is usually not detrimental to the process of the present invention and, in fact, often the presence of a thin oxide film is beneficial. In instances where considerable corrosion has taken place, it may be necessary to remove the major amount of corrosion. In general, freshly galvanized surfaces do not exhibit such a degree of corrosion as to necessitate removal of oxide film in a pretreatment.

While the process of the present invention may be used at any suitable time, it is preferred that the zinc surface be treated shortly after the zinc surfaced material or article has been manufactured. In some instances, the treatment may be successfully incorporated in the manufacturing process. For example, it is possible to incorporate the present invention in a conventional continuous galvanizing line for ferrous metal strip at any suitable stage after application of the zinc coating, provided the proper temperature conditions are met. This may be done by first cooling the molten zinc on the steel base to a temperature sufficient to solidify the same but still allow the proper temperature conditions to be met. Then, following the cooling step, the inhibitor solution is sprayed on the hot galvanized sheet. Inasmuch as the solution is substantially instantaneously evaporated, and since further treatment of the strip is not necessary or even desirable in most instances, the corrosion inhibited galvanized steel strip is then ready for coiling or packaging in the usual manner.

Corrosion inhibiting films deposited in accordance with the present invention are invisible to the naked eye, colorless in the amounts applied, and do not noticeably change the appearance of the zinc surfaced material. The resulting film is tenaciously adhered to the zinc surface in a manner suggesting chemical bonding and thus is to be distinguished in this respect from prior art chemical films. The films deposited in accordance with the present invention have been found to be very resistant to leaching and to exhibit corrosion inhibition properties over much longer periods of time than conventional chemical treatments.

In general, once a minimum amount of corrosion inhibiting film is deposited, thinner films are preferred over thicker films. For example, each square foot of surface area should be intimately contacted with a volume of solution containing a total amount between about 4.5×10^{-5} and 3.5×10^{-4} gram ion of zinc ion and chromate ion. If greater quantities of solution are used, then the corrosion inhibiting value of the film tends to deteriorate for some reason unknown at the present time and the best results generally are not obtained. If amounts of film are deposited smaller than as above specified, then in most instances a sufficient degree of corrosion inhibition is not imparted to the zinc surface to result in a superior product.

The manner in which the process of the present invention results in improved inhibition of white rusting is not fully understood at the present time. However, the following illustrative over-all reaction is presumed to take place when the solution contains zinc chloride and chromic acid :

$$ZnCl_2 + CrO_3 + H_2O \rightarrow ZnCrO_4 \downarrow + 2\,HCl \uparrow$$

It is thought that some zinc dichromate also may be formed and deposited along with the zinc chromate, and perhaps still other species of chromate may be deposited. The reaction to form zinc chromate when operating in accordance with the present invention is not believed to occur until the solution is in contact with the hot zinc surface. The zinc chromate so formed and under the conditions of the reaction then appears to react with or to be attracted to the zinc surface in some manner thereby causing the deposited thin invisible film to tightly adhere to the zinc surface in a manner suggesting chemical bonding. Whatever the theory, the process of the present invention is highly effective in inhibiting white rusting of zinc surfaces.

Although the present invention has been specifically described herein in connection with contacting an atomized solution with hot zinc surfaces, other equivalent means of application may be used. It is only necessary that the inhibitor solution be applied on the hot surface in a manner which permits the substantially immediate evaporated of volatile components. Thus, the solution may be applied by a roll or other suitable means as a thin continuous film as distinguished from a finely divided atomized spray.

The foregoing detailed description and the following specific examples are for the purpose of illustration only and are not intended as limiting to the spirit or scope of the appended claims.

Example 1.

The various samples treated and tested in accordance with the procedures of this example were prepared from galvanized steel sheet. The sample size was about 4 x 4 inches.

Each sample was treated and tested in accordance with the following general procedure :

(1) The sample was heated 10 minutes in a muffle furnace at 600° F.

(2) The sample was removed from the muffle furnace and immediately sprayed for varying periods of time (2, 4, 6, 8, 15 seconds) with aqueous test solutions of varying composition (solutions 1-7).

(3) The sample spray gun distance was 10 inches and the spray gun pressure was 10 psi, using pressurized argon as the gas source. A standard type spray gun was used and under such operating conditions the average particle size in the spray was about 10-150 microns.

(4) The treated sample was placed over tepid water and observed at intervals of 1 and 7 days Where the sample exhibited substantially no visible white rusting, the results were recorded as "Good" (G). If a small amount of white rusting was visible, or if considerable white rusting was visible, then the results were recorded as "Fair" (F) and "Bad" (B), respectively.

The aqueous solutions tested had the following compositions, with all percentages being by weight :

Solution No.	Composition
1	2-1/2% CrO_3 ; 2-1/2% Zn $(NO_3)_2$
2	5% CrO_3 ; 5% Zn $(NO_3)_2$
3	3% CrO_3 ; 3% Zn $(NO_3)_2$; 3% Mg $(NO_3)_2$
4	3% CrO_3 ; 3% Zn $(NO_3)_2$; 3% Al $(NO_3)_3$
5	3% CrO_3 ; 3% Zn $(NO_3)_2$; 3% Co $(NO_3)_2$
6	3% CrO_3 ; 3% Zn $(NO_3)_2$; 3% Ni $(NO_3)_2$
7	2-1/2% CrO_3 ; 2-1/2% Zn $(NO_3)_2$; 2-1/2% Co $(NO_3)_2$; 2-1/2% Ni $(NO_3)_2$

The volume of solution sprayed on each 10 square inches of surface treated was determined experimentally to be 0.024 ml when the spraying time was 4 seconds. Volumes of solution for spraying times other than 4 seconds may be readily calculated from this data.

In all instances, where a white rust inhibition value of "Good" was obtained, volatile components of the atomized solution evaporated almost instantaneously after contacting the heated surface and a thin invisible corrosion inhibiting film was deposited on the heated surface. This deposited film was found to adhere to the metal surface with a tenacity suggesting chemical bonding and could not be readily leached. The samples were not discolored or otherwise adversely affected in appearance after treatment.

The results of treating and testing various samples in accordance with the above described procedure are tabulated below in Table I.

TABLE I

White Rust Inhibition

Sample Number	Solution Number	Spraying Time (Sec.) Exposure Time (days)	2 Sec.		4 Sec.		6 Sec.		8 Sec.		15 Sec.	
			1	7	1	7	1	7	1	7	1	7
1	1		G	G								
2	1				G	G						
3	1						G	G				
4	2								F			
5	2										B	
6	2				G	G						
7	2		G	G								
8	2						G	G				
9	2								F	F		
10	3		B	B								
11	3				F	F						
12	3						G	G				
13	4		F	F								
14	4				G	G						
15	4						G	G				
16	5		B	B								
17	5				F	F						
18	5						G	G				
19	6		B	B								
20	6				B	B						
21	6						G	G				
22	6								G	G		
23	7		B	B								
24	7				B	B						
25	7						F	F				
26	7								G	G		
27	Distilled Water	Bad after 1 day exposure										

B—Bad.

F—Fair.

G—Good.

It may be observed from the above data that the most satisfactory degree of white rust inhibition is obtained when using either Solution 1 or 2 and for minimum spraying times, in the case of Solution 2. In general, once a minimum amount of film to effect corrosion inhibition is deposited, then thinner films give more satisfactory results than heavier films. When using either Solution 1 or 2, a spraying time of 4 seconds is preferred in most instances.

Example II.

Samples were prepared, treated and tested following the procedure of Example I unless otherwise indicated below.

A series of test solutions having a total molar amount of zinc chloride and chromic acid of 1.0 mole were prepared. The concentrations of zinc chloride and chromic acid in the solutions were varied between 1.0 mole zinc chloride, 0.0 mole chromic acid and 0.0 mole zinc chloride, 1.0 mole chromic acid. The solutions thus prepared were sprayed on the samples using the optimum spraying time of 4 seconds. The treated samples were then tested. The results are illustrated in the drawing.

Upon reference to the drawing, it will be noted that a white rust inhibiting value of "Good" is obtained when the molar ratio of zinc chloride to chromic acid is between about 9 : 1 and 1 : 9.5, with even better results being obtained with molar ratios of zinc chloride to chromic acid between about 4 : 1 and 1 : 9. In most instances, a solution containing about equimolar amounts of zinc chloride (Zn^{++}) and chromic acid ($CrO_4^{=}$) will give superior results and is preferred.

We claim :

1. A process for treating material having a zinc surface to improve corrosion resistance comprising intimately contacting a solution comprising at least one compound which is a source of zinc ion and at least one compound which is a source of chromate ion dissolved in a volatile solvent with the zinc surface of the material, the solution containing a ratio of zinc ion to chromate ion of 9 : 1 to 1 : 9.5, the zinc surface being initially at a temperature above the boiling point of the solvent and below the melting point of zinc, the volume of solution contacted with the zinc surface being controlled and the temperature of the zinc surface being sufficiently elevated so as to volatilize the volatile components of the solution immediately after contact and produce an essentially colorless corrosion resistant film on the zinc surface.

2. A process as claimed in Claim 1, in which the solution is free of reducing agents for chromate ion.

3. A process as claimed in Claim 1 or 2, in which the volatile solvent is an aqueous solution or water.

4. A process as claimed in Claim 3, in which the initial temperature of the zinc surface is from 225°F. to 600°F.

5. A process as claimed in Claim 3 or 4, in which the initial temperature of the zinc surface is from 250°F. to 350°F.

6. A process as claimed in any of the preceding claims, in which the ratio of zinc ion to chromate ion is from 4 : 1 to 1 : 9.

7. A process as claimed in any of the preceding claims, in which the compound which is a source of zinc ion is a zinc salt soluble in the solvent.

8. A process as claimed in Claim 7, in which the zinc salt is zinc chloride or nitrate.

9. A process as claimed in any of the preceding claims, in which the compound which is a source of chromate ion is chromic acid.

10. A process as claimed in any of the preceding claims, in which the concentration of zinc ion and chromate ion totals 1 gram ion.

11. A process as claimed in any of the preceding claims, in which the volume of solution which is applied to each square foot of zinc surface treated contains initially from $4.3 \times 10_{5}$- to $3.5 \times 10_{4}$- gram ion of zinc ion and chromate ion.

12. A process as claimed in any of the preceding claims, in which the zinc surface is pretreated for removal of oils and greases.

13. A process for treating material having a zinc surface to improve corrosion resistance substantially as hereinbefore described with reference to and as illustrated in any of the Examples.

14. A material when treated by the process as claimed in any of the preceding claims.

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Agent for the Applicant.

Dated this 28th day of December 1960.

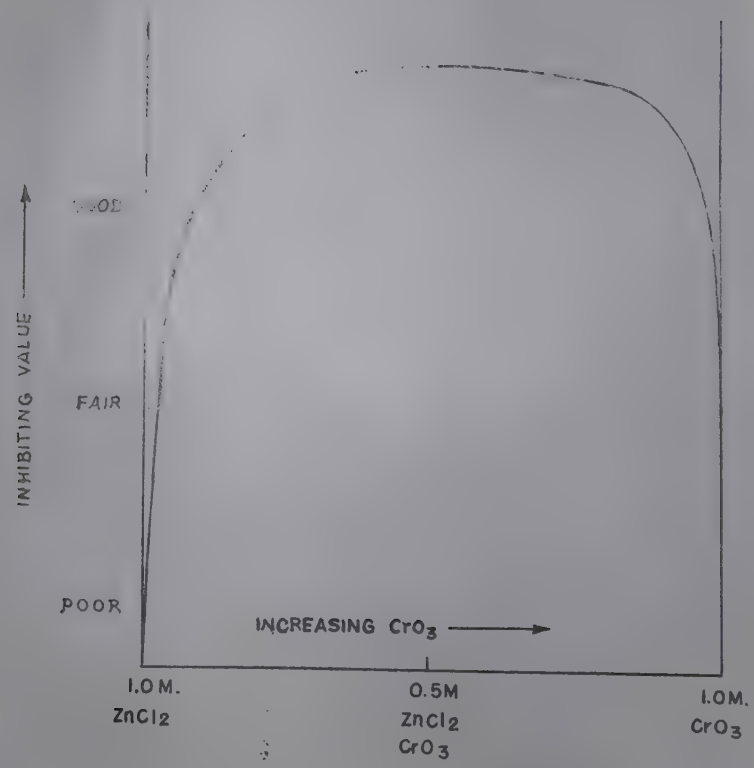
MGIP Samth.—S1.—102 Patent/62—29-4-63—100.

R. HALL.

No. 74715 of 1960.

1 Sheet

WHITE RUST INHIBITION
BY SPRAYED MIXTURES OF $ZnCl_2$ - CrO_3



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REG. NO. 2273 E'44—106'6

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(Accepted 24th September, 1962.)

ANTI-ICING ADDITIVES FOR HYDROCARBON FUELS.

PHILLIPS PETROLEUM COMPANY, A CORPORATION ORGANIZED UNDER THE LAWS OF THE STATE OF DELAWARE, UNITED STATES OF AMERICA, OF BARTLESVILLE, STATE OF OKLAHOMA, UNITED STATES OF AMERICA.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed

This invention relates to anti-icing additives for hydrocarbon fuels. In one aspect this invention relates to a liquid hydrocarbon fuel having an anti-icing additive incorporated therein. In another aspect this invention relates to a method for operating a continuous combustion type power plant using said hydrocarbon fuel.

The formation of ice within the fuel system of a jet aircraft has been recognised as a problem for a long time. Flights at high altitudes for long durations often result in the fuel being chilled to temperatures approaching that of the air in which the aircrafts are operating. All jet fuels contain small amounts of dissolved and/or entrained water. When the fuel is chilled, the water separates from the fuel and ice is formed. Ice formation in an aircraft fuel system at points of restricted flow as filters, screens, valves, and orifices, is a serious matter because the engine fuel supply may be restricted and certain instruments may not respond correctly. A number of engine flame-outs have been attributed to ice formation in the fuel system.

An obvious way to prevent fuel system icing is to keep the fuel dry. However, this is very difficult in view of different fuel sources and the large number of possibilities for contamination of the fuel with water during handling and in flight operations. In the operation of jet propelled aircraft, accumulation of water in the fuel cells or tanks occurs due to the extreme variations in temperature and pressure encountered at high and low altitudes, and also due to the constant variation in the level of fuel in said tanks caused by fuel consumption and fuel transfer from tank to tank to maintain proper distribution of load. In these variations of pressure, temperature and fuel level, moisture carried into the fuel tanks with the air is condensed. The amount of water thus accumulated is sufficient to saturate the fuel (if it were not already saturated when delivered to the aircraft) and to settle as a separate phase in the fuel tanks.

Heretofore, the problem of icing in carburetors in automotive engines and the like has been encountered leading to the phenomenon known as cold-stalling. Numerous fuel additives have been developed for solution of this problem and it would appear to be a rather obvious solution for the icing problem in jet aircraft to use an additive for the fuel which has been effective for prevention of cold-stalling. However, in the aircraft industry it is a common practice to coat the interior of the fuel cells with a resinous composition to protect the alloys used in their manufacture. It has been found that in such resin-coated fuel cells, some of the most efficient additives for prevention of cold-stalling attack the coating, causing it to soften and/or separate from the metal base. Under such circumstances, portions of the resin may be carried into fuel lines, screens, and filters and impede or block the flow of fuel to the engines.

We have discovered an anti-icing additive which comprises a blend of a saturated acyclic polyhydric alcohol (defined further hereinafter) and a glycol ether (defined further hereinafter), by the use of which additive the above mentioned problems are eliminated or substantially reduced. Thus broadly speaking, the present invention resides in (1) said anti-icing additive, (2) a liquid hydrocarbon fuel having a small but effective amount of said anti-icing additive incorporated therein and (3) a method of operating a jet engine using said liquid hydrocarbon fuel.

It was surprising and unexpected that said anti-icing additive comprising said blend of a polyhydric alcohol and a glycol ether is a much better anti-icing additive than either of (1) said polyhydric alcohol or (2) said glycol ether, when used alone. Thus, as clearly shown by the data given hereinafter, a synergistic effect is obtained when said polyhydric alcohol and said glycol ether are used in combination as an anti-icing additive.

Said combination anti-icing additive of the invention when incorporated in the fuel accomplishes at least two improvements in the operation of jet engines; (1) acts as an anti-icing agent and prevents plugging of the fuel system at points of restricted flow such as filters, valves, and orifices, due to ice formation and (2) eliminates or reduces deteriorating action on fuel tank coatings.

A further advantage of the fuel compositions of the invention lies in the ease with which a separate water phase can be removed from the fuel cells. In modern aircraft provision is made for drainage of such water phase through so-called "jiffy drains" situated at the bottom of the fuel cells. In cold climates and when operating with standard jet fuels alone, the water phase may be frozen solid, rendering such removal impossible without heating the fuel cells, a difficult and often hazardous procedure. However when operating with the fuel compositions of the present invention, at least a portion of the additive migrates from the fuel composition to the water phase in a sufficient amount to prevent freezing of said water phase even at very low ambient temperatures.

Thus according to the invention there is provided an anti-icing additive, suitable for use in a liquid hydrocarbon fuel, comprising a blend in synergistic proportions of (1) a saturated acyclic polyhydroxy alcohol containing from 3 to 5 carbon atoms, from 2 to 5 OH groups each attached to different carbon atoms and wherein the ratio of OH groups to carbon atoms is in the range of 0.66:1 to 1:1, and (2) a glycol ether having the formula $R(OCH_2CH_2)_xOH$ wherein: R is selected from the group consisting of a hydrogen atom, methyl, ethyl, propyl, butyl, phenyl and tolyl groups; when R is hydrogen, X is an integer of from 2 to 4; and when R is other than hydrogen, X is an integer of from 1 to 4.

Further according to the invention there is provided a liquid hydrocarbon fuel having said anti-icing additive incorporated therein in an amount within the range of from 0.01 to 1, preferably 0.01 to 0.5.

Still further according to the invention there is provided a method of operating a jet engine which comprises passing a liquid hydrocarbon fuel containing a small but effective amount of an anti-icing additive of the invention through the fuel supply system of said engine to a combustion zone of said engine, and burning said fuel.

As mentioned above, it was surprising and unexpected that a synergistic effect is obtained when said saturated acylic polyhydric alcohol is used in combination with said glycol ether in the anti-icing additive of the invention. In the practice of the invention, suitable proportions for said alcohol and said ether in the anti-icing additive are usually from 0.5 to 49 weight per cent of the said alcohol and from 99.5 to 51 weight per cent. of said ether. A presently more preferred range is from 1 to 40 weight per cent. of said alcohol and from 60 to 99 weight per cent. of said ether. A particularly preferred composition comprises 1 to 10 weight per cent. of the alcohol and 90 to 90 weight per cent. of the ether.

Examples of saturated acyclic polyhydroxy alcohols which can be used in the practice of the invention include the following: 1,2-dihydroxypropane; 1,3-dihydroxypropane; glycerol; 1,2,3-trihydroxybutane; 1,2,4-trihydroxybutane; 2-(hydroxymethyl) - 1,3-dihydroxypropane; erythritol; pentaerythritol; 1,2,3,4-tetrahydroxy-

Price : TWO RUPEES.

pentane; 1,2,3,5 - tetrahydroxypentane; 1,2,4,5-tetrahydroxypentane; 2-(hydroxymethyl)-1,3,4 - trihydroxybutane; and 1,2,3,4,5-pentahydroxypentane.

A presently preferred group of polyhydroxy alcohols are glycerol; 1,2,3-trihydroxy butane; 1,2,4-trihydroxybutane; and erythritol. Glycerol is the presently most preferred polyhydroxy alcohol.

Examples of said glycol ethers which can be used in the practice of the invention include, among others, the following: methyl ether of ethylene glycol (methyl cellosolve); ethyl ether of ethylene glycol (ethyl cellosolve); butyl ether of ethylene glycol (butyl cellosolve); methyl ether of diethylene glycol (methyl carbitol); ethyl ether of diethylene glycol (ethyl carbitol); butyl ether of diethylene glycol (butyl carbitol); methyl ether of triethylene glycol; ethyl ether of triethylene glycol; phenyl ether of ethylene glycol; tolyl ether of ethylene glycol; phenyl ether of diethylene glycol; tolyl ether of diethylene glycol; phenyl ether of triethylene glycol; tolyl ether of triethylene glycol; diethylene glycol; triethylene glycol; and tetraethylene glycol

A presently preferred group of glycol ethers suitable for use in the practice of the invention are those having the formula $R(OCH_2CH_2)_xOH$ wherein. R is selected from the group consisting of methyl, ethyl, propyl, and butyl groups, and X is an integer of from 1 to 4. The most preferred glycol ethers are those of the above formula wherein R is methyl or ethyl and X is 1 or 2.

The following examples will serve to further illustrate the invention.

Example I

In the engine fuel supply system of a jet aircraft the points which most frequently plug due to ice formation are the fuel filters. Thus the filter plugging characteristics of a jet-engine fuel containing an anti-icing additive are a good measure of the effectiveness of said additive as an anti-icing agent.

The filter plugging characteristics of a jet-engine fuel are tested by a procedure and employing apparatus designed particularly for this purpose. The apparatus consists essentially of a fuel reservoir system designed to supply the fuel at a constant rate to an enclosed filter cell element immersed in a constant temperature bath. Said filter cell is provided with an inlet positioned above an outlet having an effective area of 1.0 square centimeter. The filter used across said outlet is a 10 micron filter paper, Catalogue No. 74698, Precision Scientific Company. If desired, stainless steel filters of 200-300 mesh can be used instead of said filter paper. It has been found that using said 10 micron paper affords a more severe test than said 200 mesh screen. A manometer is provided to measure the pressure drop across the filter.

The fuel to be tested is admitted to the filter cell element through a copper coil so constructed that said coil and said cell element can be completely immersed in said constant temperature bath. Said coil provides for quick chilling of the fuel to the desired predetermined temperature. A thermocouple is provided for measuring the temperature of the fuel entering the filter cell. When the temperature of the cooling medium in the constant temperature bath has reached the desired predetermined temperature the flow of fuel to be tested is started. The filtrate is received in a graduated cylinder and pressure drop readings are taken for each 10 milliliters filtered so that a curve relating pressure drop across the filter and volume filtered can be plotted. A test is completed by filtering 1000 ml. of sample or reaching a pressure drop across the filter of 260 mm. of mercury (approximately 5 pounds), whichever occurs first. In this test method the filter can be considered to be plugged when the pressure drop reaches 260 mm. of mercury.

Filtration tests at −40°F. were conducted employing the jet fuel described hereinafter and which had been saturated with water at 75°F., and said water saturated jet fuel to which had been added various anti-icing additives. The results of said tests are set forth in Table I below.

Table I.

Run No.	Additive Concentration Vol.%	Additive Composition-Wt.%		Volume Filtered	Pressure Drop
		Ethylene Glycol Monomethyl ether	Glycerol	ml.	mm.Hg.
1	0.0	—	—	139	260
2	0.025	100	—	850	260
3	0.025	—	100	390	260
4	0.025	90	10	1000	100
5	0.025	75	25	1000	68
6	0.025	50	50	1000	42
7	0.010	100	—	593	260
8	0.010	—	100	282	260
9	0.010	90	10	789	260
10	0.010	98	2	958	260
11	0.010	99	1	1000	218

It is apparent from the above data a synergistic effect is obtained when ethylene glycol monomethyl ether and glycerol are used in combination as an anti-icing additive in accordance with the invention. A comparison of Runs 4, 5, and 6 with Runs 2 and 3 shows that the blends of ethylene glycol monomethyl ether and glycerol are superior to either the ethylene glycol monomethyl ether above or the glycerol alone, all additives being tested at the same concentration.

A comparison of Runs 7, 8, and 9 shows that even though the maximum pressure drop was reached in all three runs, the amount filtered in Run No. 9 is much greater when using the combination additive of the invention than when using either of the individual component additives alone as in Runs 7 and 8. All additives were again tested at the same concentration and the results again clearly show the unexpected synergistic effect. Obtained when using the combination additive of the invention.

Example II.

Actual flight tests in a B-52 jet aircraft have demonstrated the practical value of the anti-icing additives of the invention. In those tests the basic flight test procedure was to fly the aircraft at an altitude of

40,000 to 45,000 feet until the bulk fuel temperature in the fuel tanks had decreased to at least −20°F. or lower. Six flight tests of an average duration of 10 to 12 hours were made.

In three of said tests the No. 1 engine was not protected by a heater in the fuel system and was supplied from No. 1 main tank with JP-4 fuel containing approximately 100 parts per million of water. Engines Nos. 2, 3 and 4 were protected by fuel system heaters and were supplied from No. 2 main tank with JP-4 fuel containing approximately 100 parts per million of water. The remaining four engines, Nos. 5, 6, 7 and 8, were not protected with fuel system heaters. Engines Nos. 5 and 6 were supplied from No. 3 main fuel tank with JP-4 fuel containing approximately 100 parts per million of water and, in accordance with the invention, also containing 0.1 volume per cent. of an anti-icing additive consisting essentially of a blend of about 90 weight per cent. ethylene glycol monomethyl ether and about 10 weight per cent. glycerol. Engines Nos. 7 and 8 were supplied from No. 4 main tank with JP-4 fuel containing approximately 100 parts per million of water and, in accordance with the invention, also containing 0.1 volume per cent. of an anti-icing additive consisting essentially of a blend of about 90 weight per cent. diethylene glycol monomethyl ether and about 10 weight per cent. glycerol.

In the remaining three flight tests the test conditions were the same as said first three flight tests except that the fuel in main tanks 1, 3 and 4 had excess water in the amount of 2 milliliters per gallon added thereto.

Repeated fuel flow interruptions and flame-outs were experienced on No. 1 engine throughout said flight tests. The remainder of the engines functioned in normal manner. After each flight the fuel system screens were removed immediate upon landing. Ice was found on said screens and it was established that fuel system ice was responsible for the failures of No. 1 engine. No ice was found in the fuel systems of the other engines.

It was also found that the water drain valves on main fuel tanks 1 and 2 (fuel contained no additive) were frozen whereas the drain valves on main fuel tank 3 and 4 (fuel contained additive) were free and clear.

Example III.

Tests were made to determine the pumpability at −76°F. of (1) a JP-4 jet fuel which had been saturated with water at 75°F., (2) said fuel to which there had been added 12 ml. per gallon of excess water and (3) said water saturated fuel to which there had been added an anti-icing additive consisting essentially of 90 weight per cent. of ethylene glycol monomethyl ether and 10 weight per cent. glycerol. These tests were made in an apparatus like that described in Example I except that a 200 mesh stainless steel filter screen like that employed in commercial jet engines was employed in the filter cell.

In a control run, said water saturated JP-4 jet fuel showed an initial pressure change at 8°F., and when the temperature was decreased further to 6°F. the flow through the system was approximately zero.

In another control run excess water was added to said water saturated JP-4 jet fuel in an amount of 12 milliliters per gallon. In this run the initial pressure change was observed at 26°F., and when the temperature was decreased further to 23°F., flow through the system was approximately zero.

In a test run using said water saturated JP-4 jet fuel to which there had been added 0.025 volume per cent. of an anti-icing blend according to the invention consisting essentially of 90 weight per cent. of ethylene glycol monomethyl ether and 10 weight per cent. of glycerol, the pumpability of the fuel was 100 per cent. at −76°F.

This example shows that the anti-icing additives of the invention will serve to protect the fuel system of a jet engine or other continuous combustion type former plant, even when operated at temperatures as low as −76°F.

Example IV.

A series of aluminum alloy coupons measuring 1"×6", coated with different blends of Buna N (butadiene-acrylonitrile copolymer) and a phenolic resin dissolved in a solvent were evaluated in a series of tests to determine the effect of various concentrations of a blend containing 90 weight per cent. of ethylene glycol monomethyl ether and 10 weight per cent. glycerol in JP-4 jet fuel on the coatings. Duplicate coupons A and B were prepared from each coating material and tested as follows. The fuel blends were placed in glass jars in an amount such that when a coupon was placed in a jar it was about half immersed. The jars containing the coupons were then maintained in an oven at 140°F. for 14 days, the solutions being changed each day to simulate refilling of tanks in an aircraft.

Three types of evaluation were used in these tests. The first evaluation, a thumb-rubbing test was made daily. This test was qualitative only but capable of showing development of tackiness or softening of the coating. In this test all coatings were satisfactory.

The second evaluation was a pencil hardness test, made on each coupon at the end of the 14 day period. In this test, the coated surface of the coupon was marked with a pencil (A. W. Faber, Castell No. 9000) and the hardest lead that could be drawn across the coating without scratching it recorded as the pencil hardness. In this series, the hardness i designated on a scale from 1 to 20, in ascending order, based on A. W. Faber, Catell No. 9000 pencil hardness scale as follows:

1=8B	5=4B	9=HB	13=3H	17=7H
2=7B	6=3B	10=F	14=4H	18=8H
3=6B	7=2B	11=H	15=5H	19=9H
4=5B	8=B	12=2H	16=6H	20=10H

The third evaluation, made at the end of the test period, was the Scotch Tape test. The coating was scratched transversely with a steel scriber after which a piece of Scotch Tape was pressed firmly on the film and then pulled away. Softened or weakly adherent film are removed with the tape. Pencil hardness and Scotch Tape tests yielded the data shown in Table II, below.

Table II.

Run No.	Liquid Tested Composition and LV%	Coating No. 1				Coating No. 2			
		Coupon A		Coupon B		Coupon A		Coupon B	
		Pencil Hardness	Scotch Tape	Pencil Hardness	Scotch Tape	Pencil Hardness	Scotch Tape	Pencil Hardness	Scotch Tape
1	JP-4 Jet Fuel, 100%	13	OK	12	OK	13	OK	13	OK
2	JP-4+0.05% Me Cellosolve**	13	OK	12	OK	13	OK	13	OK
3	JP-4+0.05% Mixture*	13	OK	12	OK	13	OK	12	OK
4	JP-4+0.10% Me Cellosolve	12	OK	12	OK	12	OK	13	OK
5	JP-4+0.10% Mixture*	13	OK	12	OK	13	OK	13	OK
6	JP-4+0.50% Me Cellosolve	13	OK	13	OK	13	OK	11	OK
7	JP-4+0.50% Mixure*	13	OK	13	OK	13	OK	11	OK

*Methyl cellosolve-glycerol blend at 90/10 ratio as set forth above.
**Me Cellosolve=ethylene glycol monomethyl ether.

This example shows that fuels containing either or both components of the additive are not detrimental to the coatings.

Example V.

Since in service, a water phase is frequently established in the fuel cells of a jet operated aircraft, and since one or both of the components of the additive blend of the invention migrates at least partially to the water phase, a series of tests was run in which duplicate coupons coated with the coatings of Example IV were immersed in water containing methyl cellosolve, water containing glycerol, and water containing the 90/10 mixture of methyl cellosolve and glycerol. The liquid was maintained at 14[illegible] F. and the tests were run for 14 days. Pencil hardness and Scotch Tape tests were made at the end of the test period. Data from these tests are presented in Table III below.

Table III.

Run No.	Liquid Tested Composition and LV%	Coating No. 1				Coating No. 2			
		Coupon A		Coupon B		Coupon A		Coupon B	
		Pencil Hardness	Scotch Tape	Pencil Hardness	Scotch Tape	Pencil Hardness	Scotch Tape	Pencil Hardness	Scotch Tape
1	Water, 100%	10	OK	7	OK	8	Sl. Loss	7	Sl. Loss
2	Water+25% Me Cellosolve	6	OK	4	OK	3	OK	3	OK
3	Water+50% Me Cellosolve	5	Sl. Loss	6	Sl. Loss	8	OK	6	OK
4	Water+25% Glycerol	10	OK	9	OK	11	OK	8	OK
5	Water+50% Glycerol	10	OK	9	OK	11	OK	9	OK
6	Water+75% Glycerol	12	OK	11	OK	12	OK	11	OK
7	Glycerol, 100%	13	OK	13	OK	13	OK	11	OK
8	Water+25% Mixture	3	OK	7	OK	3	OK	3	OK
9	Water+50% Mixture	6	OK	5	Sl. Loss	14	OK	14	OK

These tests are considered unusually severe because all the concentrations of the various additives in water are believed to be much greater than would be encountered in actual service when the combination additives of the invention are being added to the fuel in amounts of 0.01 to 1 volume per cent.

Example VI.

A series of tests made in the manner described in Example IV was run, the liquid being a two phase system, a hydrocarbon phase (JP-4) containing 0.5 per cent. additive, and a water phase containing 50 per cent. additive. Solutions were changed daily. Tests were made on the coupons on the areas exposed to each phase. Data are shown in Table IV below.

Table IV.

Run No.	Liquid Tested Composition and LV%	Coating No. 1				Coating No. 2			
		Coupon A		Coupon B		Coupon A		Coupon B	
		Pencil Hardness	Scotch Tape	Pencil Hardness	Scotch Tape	Pencil Hardness	Scotch Tape	Pencil Hardness	Scotch Tape
1	JP-4+0.5% Me Cellosolve	13	OK	12	OK	13	OK	12	OK
2	Water+50% Me Cellosolve	11	OK	5	OK	11	OK	11	OK
3	JP-4+0.5% Mixture*	14	OK	11	OK	13	OK	11	OK
4	Water+50% Mixture*	8	OK	7	OK	8	OK	12	OK

*Methyl cellosolve-glycerol blend in 90/10 ratio as set forth above.

The above data, when compared with Runs 1 and 7 of Table II and Run 1 of Table III above, show that in two phase systems the combination additives of the invention are not detrimental to the coating materials.

Example VII.

Another series of tests was made in the manner described in Example IV except that the tests were run for a 17 day period. This series of tests was run to again simulate the conditions caused by the migration of the components of the combination additives of the invention into the water phase in the fuel cells or tanks of the aircraft when in service. The tests were run in triplicate using coupons coated with either coating composition No. 3 or coating composition No. 4. Said coating compositions Nos. 3 and 4 were of the same general type as coating compositions No. 1 and 2 of Examples III, IV and V. In carrying out the tests the coated coupons were immersed in water, and in a test solution containing 25 volume per cent. methyl cellosolve, 30 volume per cent. glycerol, and 45 volume per cent. water. Results of the tests are given in Table V below.

TABLE V.

Run No.	Liquid Tested Composition LV%	Coating No. 3						Coating No. 4					
		Coupon A		Coupon B		Coupon C		Coupon A		Coupon B		Coupon C	
		Pencil Hardness	Scotch Tape	Pencil Hardness	Scotch Tape	Pencil Hardness	Scotch Tape	Pencil Hardness	Scotch Tape	Pencil Hardness	Scotch Tape	Pencil Hardness	Scotch Tape
1	Water, 100%	6	OK	7	OK	8	OK	7	NG	5	NG	5	OK
2	Water, 45% Me Cello.. 25% Glycerol, 30%	10	OK	10	OK	9	OK	9	OK	9	OK	9	OK

The above data show that the only coating failure occurred in water alone. The coating on all coupons in Run No. 2 were tight and in excellent condition. A comparison of Run No. 1 with Run No. 2 shows that with all coupons the condition of the coupons in Run No. 2 was superior to the condition of the coupons in Run No. 1.

The JP-4 jet fuel used in the above Examples I, III, IV and VI had the following physical properties:

Reid Vapor Pressure 2.20
A. P. I. Gravity 53.5

Distillation—(°F)	I.B.P.	138°F	60 per cent vaporised	367°F
5 per cent vaporised	220°F	70 ,,		363°F
10 ,,	251°F	80 ,,		383°F
15 ,,	268°F	90 ,,		417°F
20 ,,	278°F	95 ,,		445°F
30 ,,	300°F	EP		473°F
40 ,,	319°F	Rec		99%
50 ,,	326°F	Res		1%

Said fuel complied fully with all other specifications for a JP-4 jet fuel, including the freezing point specification maximum of -76°F. As is known to those skilled in the art, this freezing point specification is provided to insure that plugging of the fuel system will not occur due to freezing of the fuel itself at the low temperatures existing at the high altitudes at which jet aircrafts operate.

Any suitable type of hydrocarbon fuel can be employed in the practice of the invention. Said fuels which can be so employed include the conventional jet engine fuels which comprise a blend of hydrocarbons boiling in the range from about 100 to about 700°F., such as gas oils, kerosene, and gasolines, including aviation gasoline. Fuels of the paraffin and naphthenic type having relatively low aromatic content, i.e., not more than about 20 liquid volume per cent. aromatics, as well as fuels of the aromatic type having high aromatic contents ranging from about 20 up to about 88 per cent or higher liquid volume per cent. aromatics can be used in operating continuous combustion turbo type aircraft engines according to the practice of the invention. Hydrocarbon fuels having wide boiling range, such as JP-3, JP-4, or fuels of the kerosene type, such as JP-5, can be employed, the boiling range of these fuels generally being in the range of about 200 to about 600°F.

Thus, while the invention has been described herein with particular reference to jet engine fuels, more specifically JP-4 jet engine fuel, the invention is not limited thereto. The invention can be used with all grades of jet engine fuels. The anti-icing additive of the invention can also be used with advantage in gasolines for reciprocating engines and in diesel fuels for compression-ignition engines.

The hydrocarbon fuel compositions of the invention containing an anti-icing additive of the invention may also contain commonly used other additives such as anti-corrosion agents, oxidation inhibitors, and the like.

As used herein and in the claims, unless otherwise specified, the terms "jet engine" and "jet engine fuel" refer to and include turbo-prop, turbo-jet, ramjet and pulse jet engines, and fuels designed to be used in said engines.

We claim:

1. An anti-icing additive, suitable for use in a liquid hydrocarbon fuel, comprising a blend in synergistic proportions of (1) a saturated acyclic polyhydroxy alcohol containing from 3 to 5 carbon atoms, from 3 to 5 OH groups each attached to different carbon atoms and wherein the ratio of OH groups to carbon atoms is in the range of 0.66:1 to 1:1, and (2) a glycol ether having the formula $R(OCH_2CH_2)_xOH$ wherein R is a hydrogen atom, methyl, ethyl, propyl, butyl, phenyl, or tolyl group and, when R is hydrogen, X is an integer of from 2 to 4 and when R is other than hydrogen, X is an integer of from 1 to 4.

2. An anti-icing additive according to Claim 1, wherein said blend comprises from 0.5 to 49 weight per cent. of said polyhydroxy alcohol and from 99.5 to 51 weight per cent. of said glycol ether based on said blend.

3. An anti-icing additive according to Claim 1 or 2, wherein said alcohol is 1,2,3-trihydroxy butane, 1,2,4-trihydroxy butane or erythritol.

4. An anti-icing additive according to Claim 1 or 2, wherein said polyhydroxy alcohol is glycerol.

5. An anti-icing additive according to any of Claims 1 to 4, wherein said glycol ether is ethylene glycol monomethyl ether.

6. An anti-icing additive according to any of Claims 1 to 4, wherein said glycol ether is diethylene glycol monomethyl ether.

7. An anti-icing additive according to Claim 1, 2, 4 or 5, wherein said blend comprises 1 to 40 weight per cent. of said glycerol as the polyhydroxy alcohol and 99 to 60 weight per cent. of ethylene glycol monomethyl ether as the glycol ether based on said blend.

8. An anti-icing additive according to any one of the preceding claims, wherein said blend comprises about 10 weight pr cent. of said polyhydroxy alcohol and about 90 weight per cent. of said glycol ether, based on said blend.

9. A liquid hydrocarbon fuel containing from 0.01 to 1 volume per cent. of an anti-icing additive as claimed in any one of the preceding claims.

10. A fuel according to Claim 9, wherein said anti-icing additive is incorporated in said liquid hydrocarbon fuel in an amount of from 0.02 to 0.05 volume per cent.

12. A fuel composition for operating a jet engine, said fuel comprising a liquid hydrocarbon fuel as claimed in any one of Claims 9 to 11.

13. An anti-icing additive comprising a blend in synergistic proportions substantially as hereinbefore described with reference to any one of the Examples I to III.

14. A liquid hydrocarbon fuel containing an additive substantially as hereinbefore described with reference to any one of the Examples I to III.

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Applicants' Attorney.

Dated this 28th day of December 1960.

MGIPC—L—154 Patent/62—22-8-63—100

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74717, 28th December 1960, 7th Paus 1882 (Saka). (Accepted 28th June 1962.)

COMPOSITION FOR STIMULATION OF THE CENTRAL NERVOUS SYSTEM AND PROCESS OF PREPARATION.

AMERICAN CYANAMID COMPANY, A CORPORATION ORGANIZED UNDER THE LAWS OF THE STATE OF MAINE, UNITED STATES OF AMERICA, OF 30 ROCKEFELLER PLAZA, NEW YORK, NEW YORK, UNITED STATES OF AMERICA.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to a pharmaceutical composition and more particularly is concerned with a novel pharmaceutical composition having a stimulating effect on the central nervous system.

The present invention comprises a pharmaceutical composition containing as the active central nervous system stimulant 5-phenyl-2-methylimino-4-oxazolidinone which may be represented by the following general formula shown in Figure 1 of the accompanying drawings.

Due to the mobility of the hydrogen atom it is quite likely that this compound may also exist in several additional tautomeric forms, one of which is shown in Figure 2 of the accompanying drawings.

It is to be understood that the present invention includes within its scope the above compound in all such tautomeric forms. For ease of description, however, the compound herein is named as 5-phenyl-2-methylimino-4-oxazolidinone which is descriptive of the tautomeric form in which it is usually named and written.

In accordance with this invention there is provided a process for preparing a composition having a stimulating effect on the central nervous system of mammals which comprises admixing 5-phenyl-2-methylimino-4-oxazolidinone and a pharmaceutical carrier.

5-Phenyl-2-methylimino-4-oxazolidinone has been found to be a highly useful central nervous system stimulant. It shows a mild stimulant action and excellent anorexic action over a wide range of doses and possesses distinct advantages over other stimulant drugs such as the amphetamines and pipradrol.

Amphetamine and closely related compounds such as methamphetamine have been used as central nervous system stimulants for many years, but numerous undesirable side reactions accompany their administration. For instance, they cause more or less pronounced rise in blood pressure and there is a tendency toward developing tolerance upon continual use. The herein-described compound does not have these serious side-effects and thus is markedly superior to the amphetamines. The compound of this invention is also, even at high doses free from the undesirable adrenergic and cardiovascular actions characteristic of the amphetamines. As increasing doses of the amphetamines are given, convulsions are usually observed. The compound of this invention does not cause convulsions as the doses are increased. The compound possesses a low order of toxicity and a desirable spread between effective and lethal doses, *i.e.*, a safe therapeutic index. The compound has a greater margin of safety than pipradol which shows a rather narrow range between effective and toxic doses. Furthermore, the compound is more active than 5-phenyl-2-imino-4-oxazolidinone described in the art (Chemical Abstracts *53*, 1959 page 20709c). It is approximately 3.3 times as effective in causing a 50 per cent. increase in motor activity at a non-toxic dose. This type of test is well recognized as a useful method for the determination of stimulant activity and is described by P. B. Dews, British Journal of Pharmacology, Vol. 8, page 46 (1953) and by G. Chen, *et al*, Journal of Pharmacology and Experimental Therapeutics Vol. 127, page 241 (1959).

5-Phenyl-2-methylimino-4-oxazolidinone is a white, crystalline solid, only slightly soluble in water. It is a basic substance, soluble in aqueous mineral acid at room temperature, and in some cases forms an insoluble acid addition salt. It also dissolves in alkaline solutions.

The active compound may be used in the form of the free base or as a non-toxic acid addition salt such as the hydrochloride, sulfate, phosphate, citrate, etc. The active compound may be administered orally or parenterally and when so administered is a central nervous system stimulant at individual doses ranging from about 1 to 100 milligrams. The dosage regiment can be adjusted to provide the optimum therapeutic response. For example, several doses may be administered daily, or the dose may be proportionately reduced as indicated by the exigencies of the therapeutic situation.

For therapeutic administration this active compound may be incorporated with pharmaceutical excipients and used, for instance, in the form of tablets, drages, capsules, suppositories, liquid to be administered in drops, emulsions, suspensions, syrups, chocolate, candy, chewing gum and the like. Such composition and preparations should contain at least 0.1 per cent. of the active ingredient. The percentage in the compositions and preparations may, of course, be varied and may conveniently be between about 2 per cent. and about 60 per cent. or more of the weight of the unit. The amount of active ingredient in such therapeutically useful composition or preparations is such that a suitable dosage will be obtained. Preferred compositions or preparations according to the present invention are prepared in such a manner that a dosage unit form contains between about 1 and 100 milligrams of this compound.

Tablets, pills, drages, and the like usually contain the following: A binder such as gum tragacanth, acacia, corn starch, or gelatin. A disintegrating agent such as corn starch, potato starch, alginic acid, or the like. A lubricant such as stearic acid, magnesium stearate, talc or the like. A sweetening agent such as sucaryl or saccharin may be added, as well as a flavoring such as peppermint, oil or wintergreen, or cherry flavoring.

According to this invention the compound is prepared by the direct alkylation reaction illustrated by the following equation shown in Figure 3 of the accompanying drawings.

The alkylating agents (CH_3-Y) which are useful in this reaction include dimethyl sulfate, methyl iodide, methyl bromide, methyl p-toluenesulfonate and the like. Approximately one equivalent of the alkylating agent is generally employed. While this method is capable of producing reaction mixtures which contain several components such as unreacted starting materials, the desired mono-substituted derivative, and some disubstituted derivative, separation of the desired product in significant yield for preparative purposes is entirely feasible. This reaction is generally carried out in a solvent such as an alkanol containing sufficient acid acceptor to neutralize the acid formed. An alkali metal alcoholate is conveniently used. The temperature of the reaction may vary from about 0° to about 100°C.

The invention will be described in greater detail in conjunction with the following specific examples.

EXAMPLE 1.

5-Phenyl-2-methylimino-4-oxazolidinone.

To a solution of sodium methoxide prepared by dissloving 12.6 grams of sodium in 500 millilliter of absolute methanol is added 88 grams of 5-phenyl-2-imino-4-oxazolidinone followed by the addition of 51 milliliters of dimethyl sulfate during 25 minutes. The solution is heated at the refluxing temperature about 2 hours and

cooled. The mixture is filtered, and some unreacted starting material is collected as the insoluble fraction. The filtrate is concentrated to a thick mass of crystals, and this mixture is dissolved in 500 milliliters of 1 normal sodium hydroxide. It is then extracted with 250 and 100 milliliters portions of methylene chloride, successively. The aqueous layer, containing the desired product, is then acidified with glacial acetic acid, cooled and filtered. The solid obtained is washed with water and suspended in 550 milliliters of boiling methylene chloride and filtered to remove more unreacted starting material. The methylene chloride solution is dried over sodium sulfate, filtered and concentrated to give crude 5-phenyl-2-methylimino-4-oxazolidinone which is collected by filtration. After two recrystallizations from ethyl acetate, the product melts at 121-124°C. The crude product may also be purified by partition chromatography on a celite column.

EXAMPLE 2.

Per Tablet:		*For 10,000 Tablets:*
0.0025 g.	Active ingredient: 5-phenyl-2-methylimino-4-oxazolidinone	25. g.
0.0800	Lactose	800.
0.0100	Corn Starch (For mix)	100.
0.0075	Corn Strach (For paste)	75.
0.0000 g.		1000 g.
0.0010	Magnesium Stearate (1%)	10
0.1010 g.		1010. g.

The active ingredient, lactose and corn starch (for mix) are blended together. The corn starch (for paste) is suspended in 600 milliliters of water and heated with stirring to form a paste. This paste is then used to granulate the mixed powders. Additional water is used, if necessary. The wet granules are passed through a # 8 hand screen and dried at 120°F. The dry granules are then passed through a # 16 screen. The mixture is lubricated with 1 per cent. magnesium stearate and compressed into tablets in a suitable tableting machine.

EXAMPLE 3.

Per Tablet:		*For 10,000 Tablets:*
0.0200 g.	Active ingredient: 5-phenyl-2-methylimiono-4-oxazolidinone	200. g.
0.0800	Lactose	800.
0.0150	Corn Starch (For mix)	150.
0.0100	Corn Starch (For paste)	100.
0.1250 g.		1250. g.
0.0013	Magnesium Stearate, (1%)	12.5
0.1263 g.		1262.5 g.

The active ingredient, lactose and corn starch (for mix) are blended together. The corn starch (for paste) is suspended in 800 milliliters of water and heated with stirring to form a paste. This paste is then used to granulate the mixed powders. Additional water is used, if necessary. The wet granules are passed through a # 8 hand screen and dried at 120°F. The dry granules are then passed through a # 16 screen. The mixture is lubricated with 1 per cent. magnesium stearate and compressed into tablets in a suitable tableting machine.

We claim:

1. A composition having a stimulating effect upon the central nervous system of mammals comprising essential active ingredient 5-phenyl-2-methylimino-4-oxazolidinone and a pharmaceutical carrier and in which the active ingredient is prepared by the process set forth herein.

2. A composition according to Claim 1 which contains between about 1 and about 100 milligrams of 5-phenyl-2-methylimino-4-oxazolidinone per dosage unit.

3. A process for preparing a composition having a stimulating effect on the central nervous system of mammals which comprises admixing 5-phenyl-2-methylimino-4-oxazolidinone and a pharmaceutical carrier and in which the active ingredient is prepared by the process set forth herein.

4. A process according to Claim 3, characterized by the fact that there is admixed between about 1 and about 100 milligrams of 5-phenyl-2-methylimino-4-oxazolidinone per dosage unit.

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Dated this 28th day of December 1960.

MOIPC—L(3/8)—107 Patent/62—19-3-63—100.

No: 74717 OF 1960 ONE SHEET.

NAME: AMERICAN CYANAMID COMPANY.

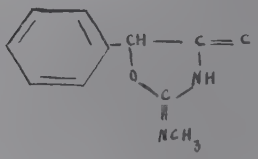

Fig 1

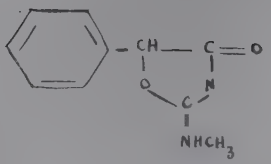

Fig 2

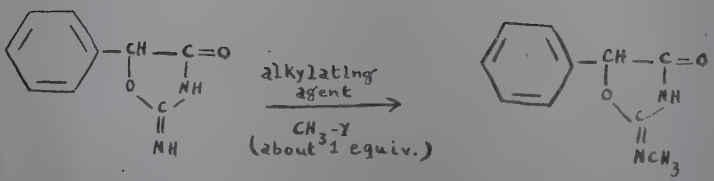

Fig 3

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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74718, filed 28th December 1960./7 Paus 1882 (Saka).

(Accepted 6th February 1962.)

"IMPROVEMENTS IN OR RELATING TO DEVICES TO SHIFT A BLOCK SIGNAL TO A GIVEN MEAN PHASE AND TO HOLD IT THEREIN WITH RESPECT TO THE PULSE INSTANTS OF AN INCOMING PULSE SEQUENCE."

N. V. PHILIPS' GLOEILAMPENFABRIEKEN, A LIMITED LIABILITY COMPANY ORGANIZED AND ESTABLISHED UNDER THE LAWS OF THE KINGDOM OF THE NETHERLANDS, CARRYING ON BUSINESS AS MANUFACTURERS AT EMMASINGEL 29, EINDHOVEN HOLLAND.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This invention relates to a device for shifting a block signal to a given mean phase and to hold it therein with respect to the pulse instants of an incoming pulse sequence. The need for such a device is particularly felt in telegraphy. The pulse sequence may then be derived from the incoming telegraph signal so that pulses correspond to the flanks of the telegraph signal. Such a pulse signal may be derived in known manner from the telegraph signal, for example, by differentiation and rectification. The problem is therein to determine as accurately as possible the centres of the code elements of the telegraph signal, since these centres indicate with the maximum probability the correct values of the code elements, so that it is of practical use to scan the original telegraph signal at the instants concerned. It is obvious that the problem is solved as soon as it is possible to produce a block signal which has, at least on an average, a given fixed phase with respect to the aforesaid pulse sequence. It is not difficult, indeed, to derive from this block signal again a pulse sequence, of which the pulses have a fixed phase position with respect to the said block signal; use is preferably made, to this end of the phase position corresponding to the centres of the telegraph signal. The device according to the invention is characterized in that it comprises a clock pulse generator of which the frequency is a multiple of the mean repetition frequency of the pulses of the incoming pulse sequence, a block-signal generator which is fed by the clock pulse generator and derives from the pulses supplied by the clock pulse generator a block signal synchronized therewith, a counting circuit, to which are fed the pulses of the incoming pulse sequence and the pulses of a pulse sequence supplied by the clock pulse generator which circuit, after the reception of a pulse of the incoming pulse sequence, counts off a fixed number of the pulses supplied by the clock pulse generator and allows them to pass, which number is, however, such that the last of a group of counted-off pulses always occurs prior to the next-following pulse of the incoming pulse sequence, a signal generator, to which both the block signal and the groups of counted-off pulses are fed, which generator is driven by the last-mentioned pulses stepwise either in one direction or in the other direction in accordance with the value of the block signal at the instant when the pulse concerned occurs and which produces a correction pulse of a first kind, when it reaches an extreme position in one direction and produces a correction pulse of a second kind, when it reaches an extreme position in the other direction, this reaching of an extreme position resulting, moreover, in that the signal generator leaps back to a central position or a zero position and in that the correction pulses produduced by the signal generator are fed to the block signal generator, which is constructed so that the block pulses of the block signal are advanced by a fixed time interval when if receives a correction pulse of one kind by and are delayed by a fixed time interval when it receives a control pulse of the other kind.

The invention will now be described more fully with reference to the accompanying drawings.

Fig. 1 shows the block diagram of one embodiment of the invention, particularly intended for the preparation of the process to which telegraph signals are to be subjected.

Fig. 2 shows a number of explanatory diagrams.

Figs. 3 to 7 show the diagrams of possible embodiments of component parts of the device shown in Fig. 1.

Referring to Fig. 1, reference numeral 1 designates a stabilized clock pulse generator having two output terminals 7 and 8, both of which supply a sequence of pulses, the pulses supplied by the terminal 7 lying, however, just midway between the pulses supplied by the terminal 8. In Fig. 2 these sequences of pulses are indicated by the graphs a and c. It is supposed that the repetition frequency of these pulses is such that one signal element of the telegraph signal corresponds, at least on an average, to sixteen pulses, but this number is not essential for the invention.

The block 2 designates a block-signal generator, which receives at its input terminal 9 the pulse sequence a and at its output terminal 10 supplies a block signal (signal b in Fig. 2). If all is correct, the centres of the blocks coincide with the high signal values coincide with the centres of the telegraph signal, which is represented in Fig. 2 by the graph b. The block signal generator 2 comprises furthermore a second output terminal 11, which supplies a sequence of pulses (signal g in Fig. 2), of which the pulses lie in the centres of the blocks with a high signal value of the block signal b. Consequently, these pulses can be used to indicate the scanning instants of the telegraph signal d. The block signal generator 2 may consist of a plurality flip-flops connected in cascade (in this embodiment four), so that from the pulse sequence a the block signals a', a'', a''' b (Fig. 2) can be derived in order of succession.

In order to permit a control, the block signal generator 2 is constructed so that it is possible to advance or to delay the block signal supplied by the output terminal 10 for a given time interval. In this embodiment this time interval is chosen to be the repetition period of the pulse sequence a and c, but this is not essential. The block signal generator 2 comprises to this end two control-terminals 12 and 13 and is designed so that the block signal b is delayed for a repetition period of the pulse sequences a and c, when a pulse h is fed to the terminal 12, and is advanced by the same time interval, when a pulse i is fed to the terminal 13. These correction pulses h and i are produced by the set of members 3 and 4.

The initial telegraph signal d (see also Fig. 2) is differentiated in a differentiator 5, so that the signal d' (see fig. 2) is obtained, this last signal being rectified in a rectifying circuit 6, which produces the pulse sequence e, which is fed to the input terminal 21 of the device as a whole. The member 3 is a counting circuit having an input terminal 14, which receives the pulse sequence c produced by the clock pulse generator 1, a control terminal 15, which receives the pulse sequence o derived from the telegraph signal d, and an output terminal 16. The counting circuit 3 is designed so that, after the reception of a pulse of the pulse sequence e, it allows a fixed number of pulses (in this embodiment nine) of the pulse sequence c to pass to its output terminal 16, after which it closes until the next-following pulse of the pulse sequence e is received. This number must at least be equal to two and is allowed to be at the most equal to the mean number of pulses of the

pulse sequence c corresponding to a signal element minus one. The conditions for obtaining the optimum control will be described more fully hereinafter.

The pulse groups supplied by the counting circuit 3 (signal f) are fed to an input terminal 17 and the block signal supplied by the block signal generator 2 (signal b) is fed to an input terminal 18 of a signal generator 4. This signal generator is a member which is caused by each pulse fed to its input terminal 17 to perform a step either in one or in the other of two opposite directions. For the sake of simplicity this will hereinafter be termed an upward step and a downward step respectively. Whether a step is performed upwardly or downwardly depends upon the fact whether the potential of the block signal b is high or low at the instant of reception of the pulse concerned. The signal generator is furthermore designed so that from a given zero position it can perform only a given number (for example 81) upward or downward steps and after it has reached an extreme position it jumps back into the zero position at the reception of a next-following pulse. If this jump back to the zero position is performed out of the extreme top position, the signal generator 4 supplies by its output terminal 19 a correction pulse h (Fig. 1) and if this jump back to the zero position takes place out of the extreme downward position, the signal generator 4 supplies by its output terminal 20 a correction pulse i. It may be desirable that none of the pulses fed to the input terminal 17 should occur at the instant when the block signal b fed to the input terminal 18 has a transition. In the device shown in Fig. 1 this is achieved by interlacing the pulses of the sequences a and c, whilst the transitions of the block signal b coincide with the pulses of the sequence a.

The device operates as follows. It is supposed that the relative positions of the block signal b and of the telegraph signal d are as shown in Fig. 2. The scanning pulses g then do not occur precisely at the centres of the signal elements of the telegraph signal, but slightly sooner, in other words, the control has to provide that the block signal b and hence the scanning pulses g should be slightly delayed. It appears, however, from Fig. 2 that three pulses of each group of nine pulses supplied by the counting circuit 3 occur at instants when the block signal b has a low value and that six of said pulses occur at instants when the block signal b has a high value. Consequently, the signal generator 4 will perform three downward steps and six upward steps during each pulse group supplied by the counting circuit 3. This is illustrated diagrammatically by the graph k of Fig. 2. The result of these measures is that the signal generator reaches, after sometime, its extreme top position and then jumps back into its zero position and at the same time produces a correction pulse h. The latter causes a delay of the block signal b for a given time interval, which means that it shifts so that the centres of the high parts of the block signal b and the elements of the telegraph signal are spaced apart from each other by a smaller distance than before. A similar effect is obtained, when the block signal is shifted to the other side with respect to the telegraph signal.

If the number of pulses of the pulse groups of the signal f is even-numbered, the device has two states of equilibrium, of which one is labile and one is stable. If the said number is an odd number, the device has no states of equilibrum and the signal generator 4 thus permanently performs steps either upwardly or down upwardly, so that the device oscillates about the state, which would be a stable state of equilibrium, if the said number were even. It is therefore advantageous to take for the said number an odd number, since the device is then prevented from staying in a labile state of equilibrium for a longer or shorter time, whilst, moreover, the deviation from the desired state is smaller than in the case of an even number. It may furthermore be proved that the optimum control is obtained, when the block length of the block signal b is rendered equal to half the length of the elements of the telegraph signal d and the number of pulses the pulse groups f is chosen so that each pulse group extends over the time of about one block of the block signal b. The device according to the invention has the advantage that it does not directly respond to each stated deviation from the desired state, but that it performs a correction only when the sum of successively stated deviations reaches a given value, which means that the device corrects the average of the stated deviations.

The invention is independent of the construction of the component parts of the device of Fig. 1. These parts may be of an electronic, an electric, an electro-mechanical and, if desired, even of a purely mechanical nature, although electronic components will be preferred in most cases. Hereinafter a description of an electronic embodiment of the components is given.

Fig. 3 shows a possible embodiment of the block signal generator 2. It comprises a particular pulse gate 24 and a counting circuit 25 consisting of four flipflops. The pulse gate 24 has two input terminals 26 and 27, two control-terminals 28 and 29 and one output terminal 30. The input terminal 26 receives the pulses of the sequence a, the input terminal 27 the pulses of the sequence c, the control-terminal 28 the correction pulses h and the control-terminal 29 the correction pulses i. Normally the pulse gate 24 allows only the pulse sequence a fed to its input terminal 26 to pass. However, when a pulse h is fed to its control-terminal 28, one of the pulses of the pulse sequence a is suppressed, which has a delaying effect on the block signal supplied by the counting circuit 25. When a pulse i is fed to the control-terminal 29, a pulse of the pulse sequence c is allowed to pass between two successive pulses of the pulse sequence a, which has an advancing effect on the block signal b, supplied by the counting circuit 25. Fig. 4 shows the principle of a potential embodiment of a pulse gate 24. It comprises three gate circuits 35, 36, 37 and two flipflops 38, 39. Normally the flipflops 38 and 39 have a position such that the gate 35 is open, i.e. allows the pulses of the pulse sequence a to pass to the output terminal 30, whereas the gates 36 and 37 are closed, i.e. do not allow the pulses of the pulse sequences a and c to pass. If the terminal 28 receives a pulse h, the flipflop 38 changes over, so that the gate 35 closes and the gate 36 opens. Then the next-following pulse of the pulse sequence a cannot reach the output terminal 30 via the gate 35 and thus is suppressed, but it passes through the gate 36, so that the flipflop 38 returns to its normal position. The following pulse of the pulse sequence a passes normally through the gate 35. Consequently, just one pulse of the pulse sequence a is suppressed. If the terminal 29 receives a pulse i the flipflop 39 changes over, so that the gate 37 becomes conductive. The first-following pulse of the pulse sequence c reaches via the gate 37 the output terminal 30, but it causes at the same time the flipflop 39 to return. Consequently, just one pulse of the pulse sequence c is interlaced between two pulses of the sequence a. The counting circuit 25 may be constructed in known manner from four cascade-connected flipflops 40, 41, 42, 43 (Fig. 5), so that the block signals a', a'', a''', b (Fig. 2) are formed successively. The block signal b of which the two polarities are utilized, can be derived from the two halves of the last flipflop 43. The scanning pulses g are formed by the criterion that they should coincide with the downward fronts of the blocking signal a''', which occur at instants, when the block signal b has its high value. The signal g can thus be derived via a gate 47 from the flipflops 42 and 43.

Fig. 6 shows the principle of a potential embodiment of the counting circuit 3. It comprises a gate 50, a circuit 51, which counts off the desired number of pulses and then supplies a pulse, and a flipflop 54. Normally the flipflop 54 occupies the position in which the gate 50 is closed. If the control-terminal 15 receives a pulse of the pulse sequence s, it changes over, so that the gate 50 is opened and the pulse of the pulse sequence c are allowed to pass to the input terminal 52 of the circuit 51. As soon as

this circuit has counted off a given number of pulses (in this case nine pulses), its output terminal 53 supplies a pulse which causes the flipflop 54 to return and thus to close the gate 50 again. The circuit 51 may, for example be a circulating shift register, which after the reception of the prescribed number of pulses supplies each time a pulse and then returns to its zero position.

Fig. 7 shows the principle of a potential embodiment of the signal generator 4. It comprises a counting circuit of five cascade connected flipflops 60, 61, 62, 63, 64, this cascade being capable of counting both forwardly, and an additional flipflop 65. The possibility of counting forwardly and backwardly is obtained in known manner by deriving the change-over pulses supplied by the flipflops either from the left-hand halves or to the right-hand halves of the flipflops. This is rendered dependent on the instantaneous value of the block signal *b* by passing the change-over pulses through gates (66 to 69, 71 to 74 respectively), which are controlled by the block signal *b*. If the block signal *b* has a high value, the gates 66 to 69 are open and the gates 71 to 75 are closed. If the block signal *b* has a low value the situation is just the reverse. The position of each flipflop is indicated by the digits 0 and 1, so that the digit 0 indicates that the left-hand half of the flipflop concerned has a low voltage and the digit 1 indicates that this half has a high voltage. If the flipflops 60, 61, ...65 occupy the positions ϵ_1, ϵ_2,... ϵ_6 ($\epsilon_1 = 0$ or 1), the position of the signal generator is indicated by the symbol ($\epsilon_1\epsilon_2\epsilon_3\epsilon_4\epsilon_5\epsilon_6$). Thus, for example, the symbol (011001) signifies that the flipflop 60, 61, 62, 63, 64, 65 occupy the positions 0, 1, 1, 0, 0, 1 respectively.

The signal generator has two zero positions, i.e. the position (111111) for moving stepwise in one direction (gates 66, 67,...70 open) and the position (000000) for moving stepwise in the other direction (gates 71, 72,...75 open).

The operation of the signal generator can be described most simply with reference to the diagrams of Figs. 8, 9 and 10. It is supposed that the signal generator starts from the position (111111), which is indicated in Fig. 8 by +0, whereas the gates 66, 67... 70 are open, the gates 71, 72,... 75 are closed. Owing to the reception of the pulses of the signal *a* the signal generator 4 passes successively through the positions indicated in Fig. 8 by +1, +2,... +31,+0. Each of the flipflops 61, 62, 63, 64 changes over, when the preceding flipflop jumps from the position 0 into the position 1. The flipflop 65 remains in the position 1, since the gate 75 is closed, so that no high voltage can be fed to the right-hand half, whereas the gate 70 does not allow the low voltage that is supplied by the left-hand half of the flipflop 64 from the position +16 on, to pass. However, when the signal generator 4 jumps from the position +31 into the position +0, the flipflop 64 supplies a pulse, which passes through the gate 76, since the flipflop 65 then occupies the position 1 and the signal *b* has its high value. The signal generator has then supplied a correction pulse *h*.

Fig. 9 shows in a similar manner which positions the signal generator passes through out when starting from the position (000000) (indicated in Fig. 9 by −0), the gates 71, 72,... ...75 being open. Each of the flipflops 61, 62, 63, 64 changes over, when the preceding flipflops jumps from the position 1 into the position 0. The flipflop 65 remains in the position 0, since the gate 70 is closed, so that no high voltage is fed to the left-hand half of the flipflop 65, whereas the gate 75 does not allow to pass the low voltage supplied by the right-hand half of the flipflop 64 from the position −16. When the signal generator jumps from the position −31 into the position −0, the flipflop 64 supplies a pulse, which passes through the gate 77, since the flipflop 65 then occupies the position 0 and the signal *b* has its low value. The signal generator has thus supplied a correction pulse *i*.

Fig. 10 illustrates the process evolving when the signal generator starts from the position −0 and receives each time three pulses at a low value of the signal *b* (gates 71, 72,...75 open) and six pulses at a high value of the signal *b* (gates 66, 67,...70 open). After the foregoing it is not difficult to explain this diagram. It should be noted that the presence of two zero positions results in that the signal generator 4 operates in a slightly different manner from that described with reference to figures 1 and 2 as long as the signal generator swings about its two zero points. Fig. 2k is based on the supposition that the signal generator has only one zero position.

The invention is not restricted to the embodiments described above of the components. The pulses may, for example, be non-electrical; they may, for example, be pressure pulses of a gas or impacts of a rod. The various counting circuits may, if desired, be pawl-machanism-driven mechanical counters or counters driven by series-connected magnets. As far as the signal generator 4 is concerned, it may, as an alternative, be designed as a member (for example a rod or wheel) capable of moving stepwise in one or in the other of two directions and supplying, when reaching an extreme position in one direction or in the other, an electrical or mechanical pulse, for example by the transient closure of a contact or by the transient opening of a cock in a pressure duct. Then the member has to jump back into its initial position. Such a purely mechanical or electromechanical signal generator could be readily built up along known principles. However, if the occurring frequencies are comparatively high which is the case in automatic telegraphy, an electronic design of the components will mostly give the optimum solution.

WE CLAIM :—

1. A device for shifting a block signal to a given mean phase and to hold it therein with respect to the pulse instants of an incoming pulse sequence, characterized in that the device comprises a clock pulse generator (1), of which the frequency is a multiple of the mean repetition frequency of the pulses of the incoming pulse sequence, a block signal generator (2), which is fed by the clock pulse generator (1) and forms a block signal from the pulses supplied by the clock pulse generator in synchronism herewith, a counting circuit (3), to which the pulses of the incoming pulse sequence as well as the pulses of a pulse sequence supplied by the clock pulse generator are fed and which circuit, after the reception of one pulse of the incoming pulse sequence, counts off and allows to pass each time a fixed number of the pulses supplied by the clock pulse generator, this number being however such that the last of a group of counted pulses always occurs before the first-following pulse of the incoming pulse sequence, a signal generator (4), to which both the block signal and the groups of pulses counted off are fed and which generator is driven by the last-mentioned pulses stepwise either in one direction or in the other direction in accordance with the value of the block signal at the instant of occurrence of the pulse concerned and which generator produces a correction pulse of a first kind when reaching an extreme position in one direction and supplies a correction pulse of a second kind when reaching an extreme position in the other direction and in that the attainment of an extreme position moreover results in that the signal generator jumps back into a central position or zero position and in that the correction pulses produced by the signal generator (4) are fed to the block signal generator (2), which generator is designed so that the block pulses of the block signal owing to the occurrence of the correction pulse of one kind are advanced by a fixed time interval and owing to the occurrence of a control-pulse of the other kind are delayed by a fixed time interval.

2. A device as claimed in Claim 1, characterized in that the clock pulse generator (1) produces two interlaced pulse sequence and in that the block signal generator (2) consists essentially of circuit (25), which derives by frequency division a block signal from pulses fed thereto, which circuit is fed via a particular gate circuit (24) by the clock pulse generator (1), the particular gate circuit (24) , being designed so that normally it passes only the first of the two pulse sequences produced by the clock pulse generator (1), but at the reception of a correction pulse of the first kind it retains one pulse of

the said pulse sequence and at the reception of a correction pulse of the second kind it interlaces one pulse between two pulses of the normally passed pulse sequence.

3. A device as claimed in Claim 2, characterized in that the particular gate circuit (24) comprises two gates (35, 36) controlled by a flipflop (38) so that always one of these gates is open and the other is closed, whilst the first of these gates, in the open state feeds the first pulse sequence to the output terminal (30) of the gate circuit and the second of these gates, in the open state, transfers a pulse of this pulse sequence to a control-terminal of the flipflop, which thus moves to the position in which the first gate is open and in that the particular gate circuit comprises a third gate (37), governed by a second flipflop (39), which gate passes, in the open state, a pulse of the second pulse sequence to the output terminal (30), which pulse is, moreover, fed to a control-terminal of the second flipflop, which thus moves into the position in which the third gate is closed and in that a second control-terminal of each of the two flipflops is connected to a control-terminal (28, 29) of the particular gate circuit.

4. A device as claimed in Claim 1, characterized in that the number of pulses each time counted off by the counting circuit (3) is odd.

5. A device as claimed in Claim 1, characterized in that the period of the block signal is substantially equal to the mean duration of the shortest time interval between the pulses of the incoming pulses and in that the number of pulses counted off by the counting circuit is so high that each pulse group supplied by this counting circuit has a duration which corresponds approximately to half a period of the block signal.

6. A device as claimed in Claim 1, characterized in that the signal generator (4) comprises a binary counting circuit, which counts forwardly or backwardly in accordance with the value of the block signal (b), after which provision is made of a flipflop (65), which is governed by the last flipflop (64) of the counting circuit and by the block signal so that it occupies a different position one on both sides of two positions of the counting circuit, considered as zero positions, the two zero positions differing from each other by just one counted pulse and in that, when jumping back into the zero position in question via an extreme position of the counting circuit, the signal generator produces a correction signal (h or i), which is derived from the last flipflop (64) of the counting circuit, since the outputs of this flipflop are connected via gates (76, 67) to outputs (19, 20) of the signal generator as a whole, which gates are governed by the block signal (b) and by the additional flipflop (65) referred to above.

B. DePENNING
of CANTWELL & CO.
Agent for the Applicants.

Dated this 28th day of December 1960.

Printed by The Nalya Printing Works, Calcutta-1.

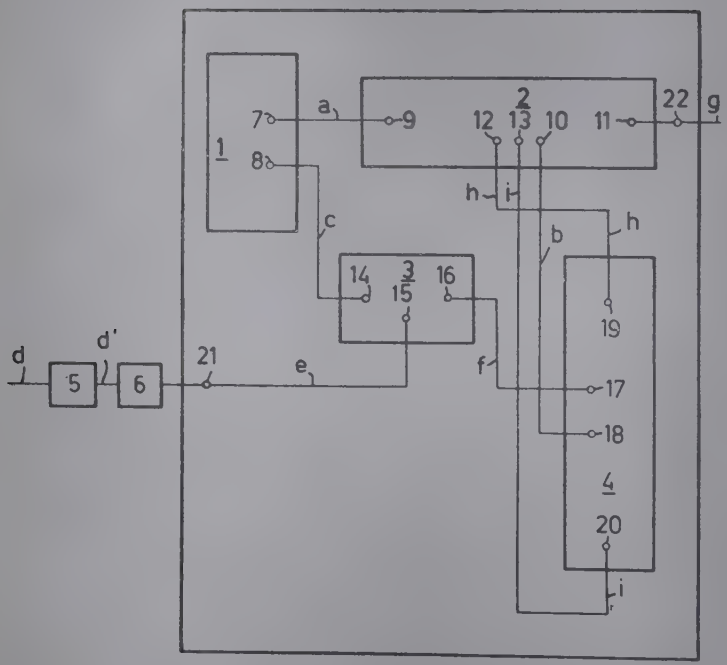

FIG. 1

B. Wilkenning
of CANTWELL & CO.
Agent for the Applicants.

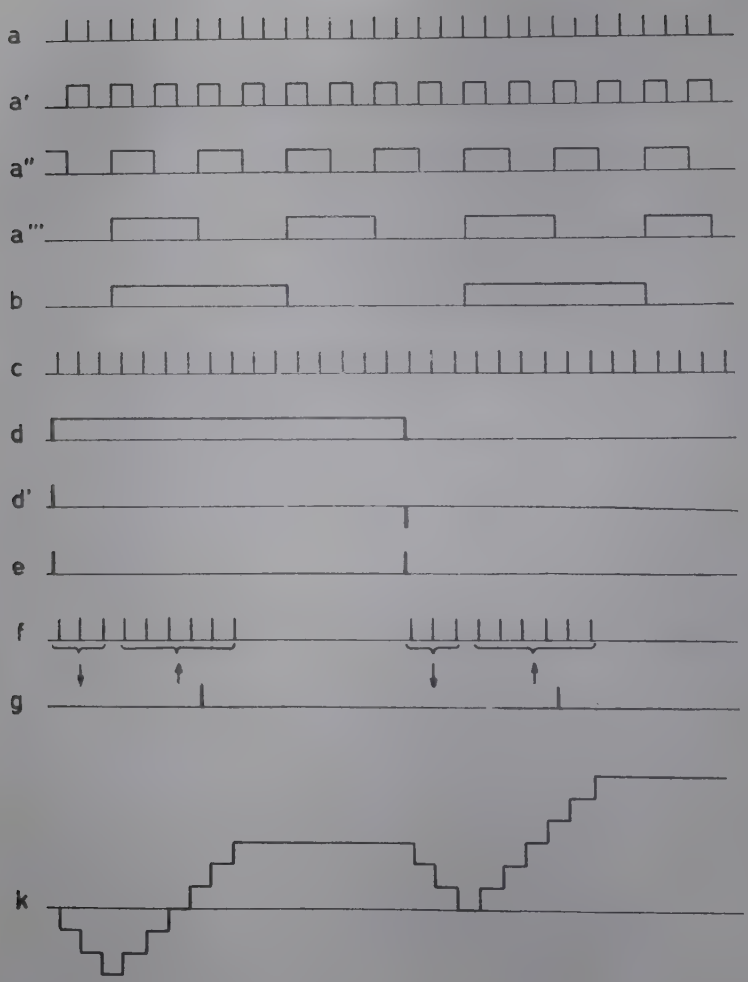

FIG. 2

B. de Penning
of CANTWELL & CO.
Agent for the Applicants.

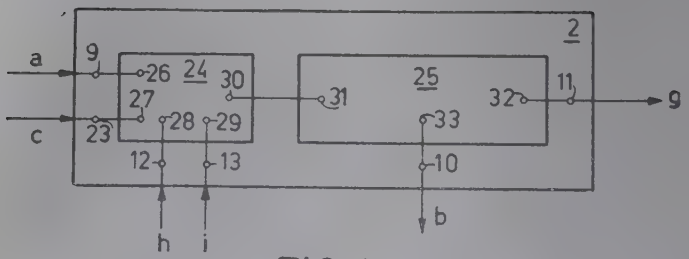

FIG.3

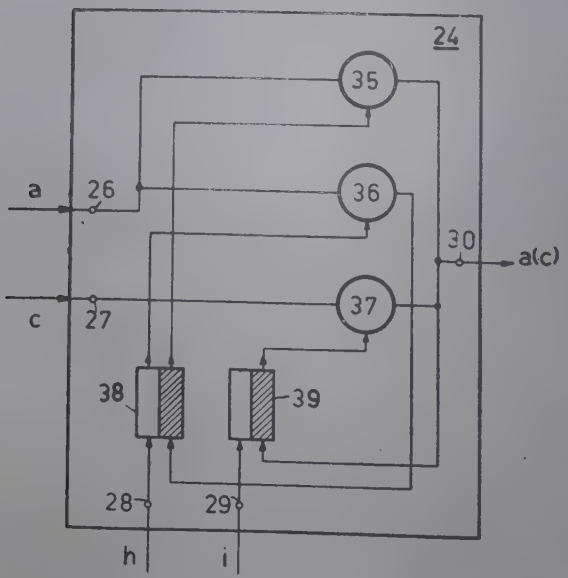

FIG.4

B. Wetsenning

of CANTWELL & CO.
Agent for the Applicants.

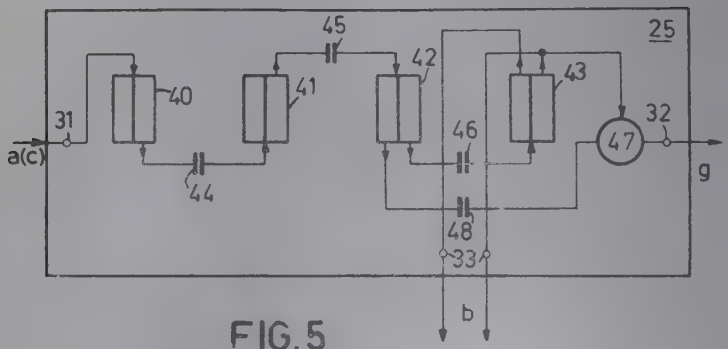

FIG.5

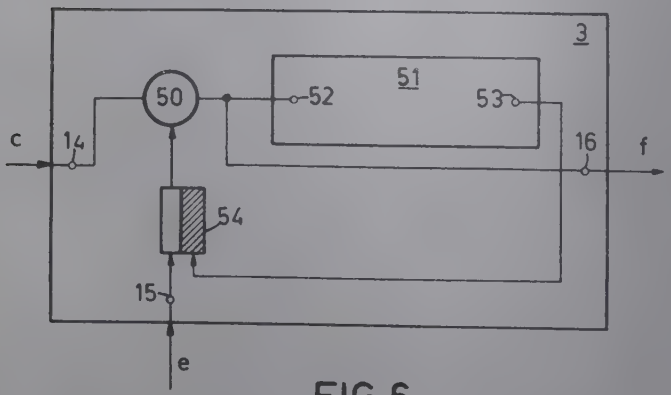

FIG.6

B. de Penning
of CANTWELL & CO.
Agent for the Applicants.

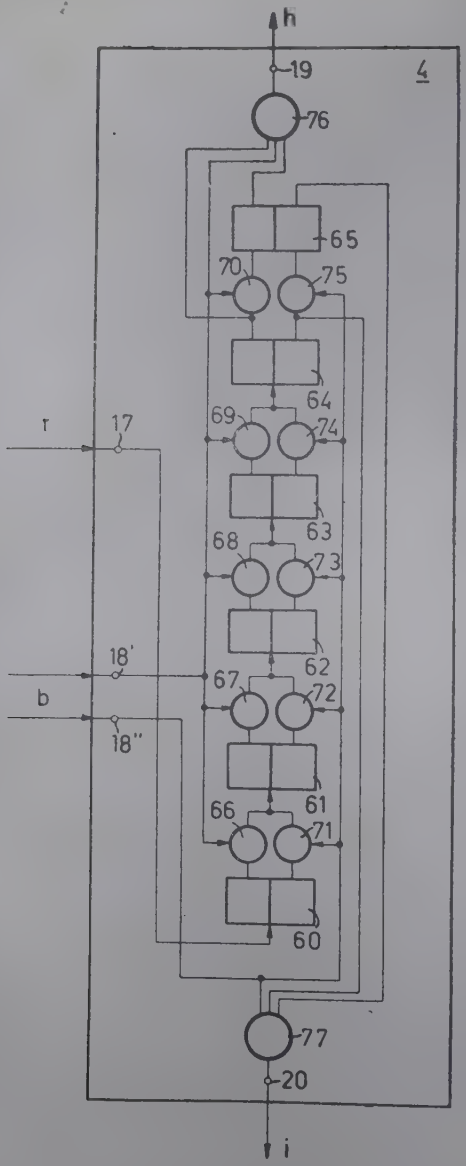

FIG. 7

B. de Penning
of CANTWELL & CO.
Agent for the Applicants.

| | | |

... INSPECTION CENTRE

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74719. filed 28th December 1960./7 Paus. 1882 (Saka)

(Accepted 26th February 1962.)

" IMPROVEMENTS IN OR RELATING TO ELECTRIC LAMPS. "

N. V. PHILIPS' GLOEILAMPENFABRIEKEN, A LIMITED LIABILITY COMPANY ORGANIZED AND ESTABLISHED UNDER THE LAWS OF THE KINGDOM OF THE NETHERLANDS, CARRYING ON BUSINESS AS MANUFACTURERS AT EMMASINGEL 29, EINDHOVEN, HOLLAND.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This invention relates to electric lamps in which a thin-walled metallic screen, positioned transversely to the axis of the lamp, is arranged on the stem tube and preferably in a cut provided therein. said screen engaging the outer side of the stem tube at the opposing inner sides of an elongated recess provided in the screen. Such a metallic screen, which the used more particularly in lamps of a comparatively high wattage, serves to protect the connection between the bulb and the lamp cap secured thereto from excessive heating. Such heating could, for example, give rise to the material used for the concoction, which is usually cement from losing its joining action and this could result in the lamp becoming defective.

It is common practice to use metallic plates for such screens, which have a bent peripheral portion of slightly resilient properties at each of the longitudinal edges of the recess. Such a structure has the disadvantage that the bending of such peripheral portions implies an additional operation in the manufacture of the screens and, furthermore, that it is impossible to obtain the screens wholly flat, that is to say without projecting parts.

An object of the present invention is to mitigate those disadvantages.

For this purpose, an electric lamp according to the invention is characterized in that at the side of at least one longitudinal edge of the elongated recess, and at a small distance from this longitudinal edge, the screen has a second recess which is wholly surrounded by the material of the screen and of which the boundary adjacent the first recess extends at least substantially parallel to the anjacent longitudinal edge of the first recess.

By following this procedure, a narrow strip of material having a certain resilience is formed in the material of the screen at the side of the relevant longitudinal edge. When a metal screen thus formed is slipped on to a stem tube, the material of the said strip, when the sidest portion of the stem tube has passed the end of the second recess adjacent the entrance aperture of the first recess, will be deformed slightly resiliently, this producing in the material of the screen a force adjacent the first recess, whice force serves to clamp the screen on the stem tube. If desired, such an additional recess could be provided at each side of the first recess. The further configuration of the second recess is only of minor importance. As a rule, because of a simplified manufacture of the screens, a rectangular periphery for the second recess will be preferred, or it will be formed preferably as a straight cut in the material of the screen.

As previously mentioned, in one advantageous embodiment of the invention, the screen may be wholly flat at least before being mounted on the stem tube. This also facilitates *inter alia* the possibility of stacking the individual screens, which circumstance may play an important part in the automated supply of the screens to the area where they are mounted on the associated stem tubes in the manufacture of the lamps.

In another embodiment of the invention, the lamp is characterized in that, while a second recess is provided only in the vicinity of one longitudinal edge of the first recess, the longitudinal edge of the first recess remote from the second recess in the screen shows a bend, preferably whilst forming a large obtuse angle, which bend is such that the first recess has a widened entrance portion, said bending point being located, as reckoned in the direction of slipping the screen onto the stem tube, at a smaller distance from the closed end of the first recess than the end of the second recess adjacent the entrance portion of the first recess.

The present invention is important both for lamps in the form of incandescent lamps and for lamps in which the light source comprises a discharge tube housed in a bulb.

In order that the invention may by readily carried into effect, it will now be described in detail, by way of example, with reference to the accompanying diagrammatic drawing, in which :

Fig. 1 shows diagrammatically and in side view one embodiment of a lamp according to the invention ;

Fig. 2 is a perspective view of the manner in which the screen may be slipped onto a stem tube provided with a cut ;

Fig. 3 is a plan view and in part section, on an enlarged scale, of the screen of Fig. 2 slipped onto the stem tube.

Flg. 4 is a plan view of a variant of a screen according to the invention.

The lamp shown in Fig. 1, which has a wattage of, for example, 250 watts, comprises a gas-filled bulb 1 and a metallic screw-cap 2 which is secured to a narrowed portion 3 of the neck of the bulb with the aid of a cemented connection (not shown). The bulb 1 contains the usual stem tube 4, the lower end of which is deformed to a pinch 5. Sealed into the pinch 5 are two current-supply wires 6 and 7 which merge into supporting wires 8 and 9, the ends of which support a filament 10. The lamp is provided with a supporting rod 11, the lower end of which merges into a knob 12. Supporting wires 13, 14 and 15 for the filament 10 are mounted in the knob 12. Portions 16 and 17 of the current supply wires, which extend within the stem tube 4, may be formed as safety fuses. In addition, the metallic lamp cap 2 is usually covered internally with an insulating layer (not shown). The pinch 5 also contains an exhaust tube 18.

In order to protect the junction of the bulb and the lamp cap from excessive heating, the lamp shown is provided in known manner with a heat screen 19 which, in this example, consists of iron sheet of 0.25 mm thick. In order to fix the correct portion of the screen on the stem tube, the latter is provided with a cut in each of its opposing sides, one cut being indicated by 20 in Fig. 2.

The screen and its co-operation with the stem tube will now be considered with reference to Figs. 2 and 3. The screen 19 in this embodiment has a first elongated recess 22, having two longitudinal edges 23 and 24 and a closed end 25. As can be seen more particularly from Fig. 2, the longitudinal edge 23 of the recess 22 has a bend at point A. Consequently, the portions of the longitudinal edge 23 form a large obtuse angle *a* having a value of, for example, 160°. The presence of the resulting widened entrance portion of the first recess 22 assists in slipping the screen onto the stem tube.

In this embodiment, the screen has, at a small distance from the other longitudinal edge 24 of the first recess, a second recess 26 which is wholly surrounded by the material of the screen and which, in this example, has a rectangular shape. In this embodiment, the distance b between the adjacent edges 24 and 27 of the first recess 22 and the second recess 26, respectively, is about 1 mm. A small strip of material 28 is thus obtained between the two recesses.

The dimension c between the relatively parallel portions of the boundary edges 23 and 24 the distance d between the deepest portions of the cuts 20 and 21 provided in the stem tube 4 are so chosen with respect to one another that the distance c is a little smaller than the distance d prior to slipping the screen 19 onto the stem tube 4. This implies, assuming that the material of the stem tube 4 is not deformable in practice, that the screen is deformed upon sliding the screen 19 onto the stem tube. This possibility of deformation is obtained due to the presence of the strip of material 27 which is deformable slightly resiliently. As previously mentioned, the thickness of the material of the screen, as indicated by c in Fig. 2, is 0.25 mm and the width b of the strip 28 is 1 mm. With respect to the load which occurs on the strip of material when the screen is provided, said strip may be regarded as a rod of rectangular cross-section clamped at two sides and having its largest dimension parallel to the load occurring. The strip of material, as can be seen from Fig. 3, will be deformed slightly resiliently and thus provide the force required for clamping the screen on the stem tube.

As may likewise be seen from Fig. 3 the distance between the bending point A and the crosed end 25 of the recess 22 has a value f, as measured in the direction of slipping B. As measured in the same direction, the distance between the closed end 29, which is adjacent the entrance side of the first recess 22, and the closed end 25 of the first recess 22 has a value g, which value g is higher than f. Consequently upon slipping the screen onto the stem tube, the stem tube first passes that portion of the longitudinal edge 24 of the recess 22 which lies directly opposite the end 29 of the recess 26 and only then passes the bending point A provided on the longitudinal edge 23 of the recess 22. As a result thereof, the slipping operation does not cause any difficulty. In addition, when the stem tube has passed the bending point A, the boundary edge 23 acquires at point A, due to the forces occuring, a cam-like deformation 30 as shown in dashed line with some exaggeration, which deformation renders it difficult for the screen to slide off the stem tube again.

It has been found that an extremely simple and efficacious method of securing the screen, which is simple in itself, to the stem tube is thus obtained.

In the embodiment of the screen shown in Fig. 4, the screen has a first recess 35, longitudinal edges 36 and 27 of which are each wholly straight and extend in parallel throughout their length. In this embodiment, a segment-shaped recess 38 is provided. In this example also a narrow strip of material 40, resiliently deformable, is present between a boundary 39 of the recess 38, which is adjacent the first recess 35, and the longitudinal edge 36 of the first recess 35.

In the embodiment shown in Figs. 1, 2 and 3, the screen is arranged on the initially cylindrical portion of the stem tube 4. It will be evident that it is also possible to arrange the screen on another portion of the stem tube, for example on the pinch 5. In this case, the first recess in the screen must, of course, be narrower. If desired, the sides of the pinch may be provided with one or more rigdes or cams in order to fix the position of the screen in a direction at right angles to the axis of the lamp.

WE CLAIM :—

1. An electric lamp in which a thin-walled metallic screen, positioned transversely to the axis of the lamp, is arranged on the stem tube and preferably in a cut provided therein, said screen engaging the outer side of the stem tube at the opposing inner sides of an elongated recess provided in the screen, characterized in that at the side of at least one longitudinal edge of the elongated recess, and at a small distance from this longitudinal edge the screen has a second recess which is wholly surrounded by the material of the screen and of which the boundary adjacent the first recess extends at least substantially parallel to the adjacent longitudinal edge of the first recess.

2. An electric lamp as claimed in Claim 1, characterized in that the screen is wholly flat at least before being mounted on the stem tube.

3. An electric lamp as claimed in Claim 1 or Claim 2, characterized in that, while a second recess is present only in the vicinity of one longitudinal edge of the first recess, the longitudinal edge of the first recess remote from the second recess in the screen has a bend, preferably whilst forming a large obtuse angle, which bend is such that the first recess has a widened entrance portion, said bending point being located, as reckoned in the direction of the slipping the screen onto the stem tube, at a smaller distance from the closed end of the first recess than the end of the second recess adjacent the entrance portion of the first recess.

4. An electric lamp, substantially as herein described with reference to the accompanying drawing.

B. DePENNING
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Agent for the Applicants.

Dated this 28th day of December 1960.

Printed by The Nelys Printing Works, Calcutta-1.

N.V.Philips' Gloeilampenfabrieken.
No. 74719.

One Sheet.

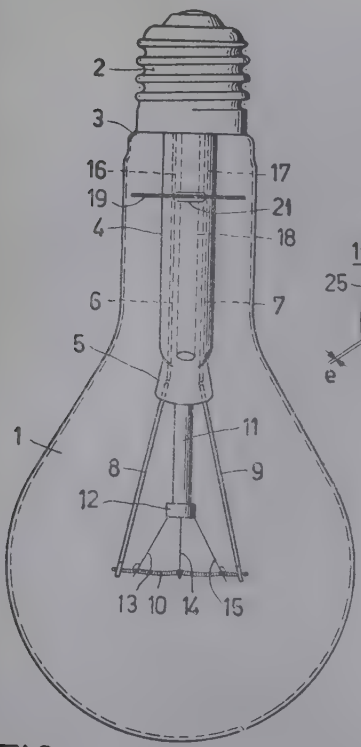


FIG. 1

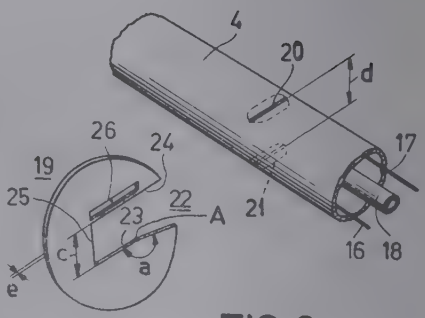


FIG. 2

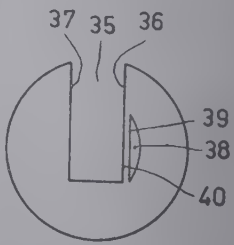


FIG. 4

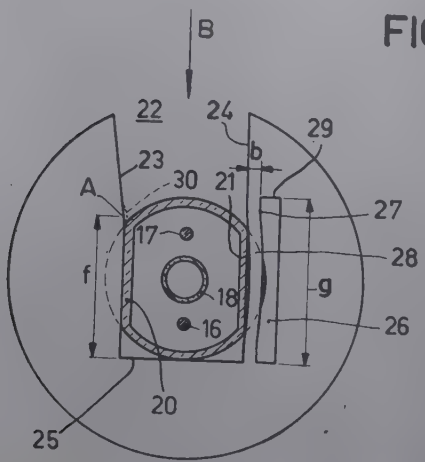


FIG. 3

B. W. Cunning.
of CANTWELL & CO.,
Agents for the Applicants.

CENTR

GOVERNMENT OF INDIA : THE PATENT OFFICE 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74720, filed 28th December 1960 / 7 Paus 1882 (Saka).

(Accepted 17th February 1962.)

" SLIDE FASTENERS. "

TADAO YOSHIDA, of 339, Suwadacho-2-chome, Ichikawa-shi, of Japanese Nationality.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

The present invention relates to slide fasteners and particularly to slide fasteners of the type which includes a pair of interlocking slide fastener elements each made from a continuous wire or filament of metal, synthetic resin or other suitable material and having a series of interconnected coil links or U-shaped links.

The present invention has for its primary object to provide an improved slide fastener having fastener elements adapted to be secured to respective carrying tapes in proper locking position against misalignment or dislocation with respect thereto and thus to secure positive and dependable interlocking engagement between the fastener elements.

According to the present invention, there is provided a slide fastener comprising a pair of interlocking fastener elements each made from a continuous filament and having a series of interconnected coil links or U-shaped links with or without a spacer element embraced therebetween, said fastener elements each being sewn on to respective supporting tapes and having a braided bead formed by doubleloop stitching so as to extend over the links of the fastener element.

Another object of the present invention is to provide a slide fastener of the type described having fastener elements not subject to impairment during heat treatment in the finishing operation of the fastener.

A further object of the present invention is to provide a slide fastener of the type described having an improved decorative effect.

A still further object of the present invention is to provide a slide fastener which is highly robust and may be efficiently produced with low cost.

These and other objects and advantages will be apparent from the following detailed description of the present invention with reference to the accompanying drawings which illustrate preferred embodiments of the invention and in which :

Fig. 1 is a front view of a slide fastener having coiled interlocking elements made from a wire or filament and secured to respective supporting tapes by double-loop stitching ;

Fig. 2 is a rear view of same ;

Fig. 3 is an enlarged cross-sectional view of the slide fastener shown in Figs. 1 and 2 taken through the slider on the fastener to show the detail of the sewing stitches and the interlocking relationship of the fastener elements ;

Fig. 4 is a front view of one of the interlocking elements in Figs. 1 to 3 ;

Fig. 5 is a side view of same ;

Fig. 6 is an end view of same ;

Fig. 7 is a front view of a modification of the slide fastener embodying the present invention having interlocking elements made of a wire or filament and each including a series of U-shaped links secured to the supporting fabric by double-loop stitching ;

Fig. 8 is a rear view of same ;

Figs. 9, 10 and 11 are views similar to Figs. 4, 5 and 6, respectively, showing one of the interlocking elements shown in Figs. 7 and 8 ;

Figs. 12, 13 and 14 are cross-sectional views similar to Fig. 3, illustrating various ways in which the fastener elements shown in Figs. 9, 10 and 11 are secured to respective supporting tapes by double-loop stitching.

Referring to the drawings, and particularly to Figs. 9, 10, 11 and 12, a slide fastener element E has a series of U-shaped links 3 interconnected by bridge portions 2 each having a locking head 2, and is positioned along one edge 1' of a supporting tape 1 with the U-shaped links extending alternately over opposite sides of the supporting tape 1. A braid or cord 4 is placed on one side of the links 3 of the fastener element E and two sewing threads 5 and 6 are employed to secure the braid 4, the fastener element E and the supporting tape 1 together into an integral assembly, one of said threads 5 extending through the supporting tape 1 to the rear side of the braid 4 to sew the individual U-shaped links 3 securely to the tape while the other thread 6 forms a braided bead 7 together with the thread 5 on the outer surface A of the U-shaped links 3 opposite to the braid 4. The fastener element E together with a companion fastener element constitutes a slide fastener adapted to be opened and closed by a slider 8 for interlocking such fastener elements. It will be noted in this connection that the slider 8 is slidable along the bight portions 3' of the respective links of the fastener elements, substantially not engaging the braided bead 7.

In another embodiment of the present invention, a spacer element 10 such as a narrow tape or a cord of circular cross section is embraced between the opposing series of U-shaped links 3 of the fastener element E having locking heads 2, said fastener element E being positioned on a supporting tape 1 along one edge thereof and sewed thereto by a pair of threads 5 and 6, one of which threads 5 extending to the rear side of the supporting tape 1 to hold the individual U-shaped links 3 in place thereon, while the other thread 6 forms a braided bead 7 together with the thread 5 on the outer surface A of the U-shaped links 3 opposite to the supporting tape 1 thereby to secure the fastener elements E; the supporting tape 1 and the spacer element 10 together into an integral assembly. Such assembly together with a similarly constructed companion assembly forms a slide fastener operable by a suitable slider 8 (see Fig. 13). It will be observed that the slider 8 is slidable along the bight portions 3' of the U-shaped links of the cooperating fastener elements E.

A further embodiment of the present invention employs supporting tapes 1 each having a bifurcated or Y-shaped cross-section along one edge thereof, one leg 1 of the bifurcated tape edge being embraced between opposing series of U-shaped links 3 on the associated one of a pair of fastener elements E, which each carries locking heads 2 (see Fig. 14), the U-shaped links 3 on one side being thus fitted in the bifurcation B of the tape while being covered along

Price : TWO RUPEES.

the outer side by the other leg 1" of the bifurcation B. Two threads 5 and 6 are employed to secure the supporting tape 1 and the fastener element E together into an integral assembly, one of the threads 5 being sewn to extend through the legs 1' and 1" of the bifurcated tape edge to the underside thereof to secure the individual U-shaped links 3 to the supporting tape 1 while the other thread 6 forms a braided bead 7 together with the thread 5 on the outer surface A of the U-shaped links opposite to the outer leg 1" of the bifurcated tape edge so as to extend over the U-shapad links. It will be understood that a mating pair of such assemblies forms a slide fastener operable by a suitable slider 8 as with the case of the previous embodiments.

A fourth embodiment of the present invention comprises a mating pair of coiled interlocking fastener elements having a series of coil links or diagonal U-shaped links interconnected by bridge portions each including a locking head or tooth 2, the legs 3 of each U-shaped link being so arranged that one leg of each U-shaped link is laterally aligned with the other leg of the adjacent U-shaped link, as clearly shown in Figs. 4, 5 and 6. The fastener element in this modification is positioned, as shown in Fig. 3, on one side of a supporting tape 1 along one edge thereof and securely sewn on to the supporting tape by use of two threads 5 and 6, one of which threads 5 being stitched to extend to the rear side of the tape 1 to hold the individual diagonal U-shaped links 3 in place thereon, while the other thread 6 forms together with the thread 5 a braided bead 7 on the outer surface A of the U-shaped links 3 opposite to the supporting tape 1 so as to extend over the U-shaped links, thereby to secure the fastener element and the supporting tape together into an integral assembly. It will be a mating pair of such assemblies forms a slide fastener operable by a suitable slider 8 adapted to interlock and release the fastener elements with and form each other (see Figs. 1, 2 and 3).

It will be apparent from the foregoing description of the several embodiments of the present invention that positive and dependable interlocking of mating fastener element is ensured by the invention by employing a spacer element such as a tape of flat section or a cord of circular section embraced between opposing links of each of the fastener elements and sewn on to a supporting tape therefor or by simply employing coiled interlocking fastener elements each sewed on to a supporting tape without no spacer element embraced between the links of the fastener element.

It will be appreciated that the present invention has among others a distinctive feature that in sewing fastener elements to respective supporting tapes two threads are used to form a braided bead on the exposed surface of the fastener element to cover the links thereof, whereby the fastener element is protected from any impairment during heat treatment in the finishing operation of the fastener, the braided bead assisting together the fastener element and the supporting tape while improving the appearance of the finished slide fastener, It will also be appreciated that such construction provides a slide fastener of the kind described which is highly robust and facilitates the production of the slide fastener compared with slide fasteners of conventional construction.

I CLAIM :—

1. A slide fastener comprising a pair of interlocking fastener elements each made from a continuous filament and having a series of interconnected U-shaped links, said fastener elements each being sewn on to respective supporting tapes and having a braided bead formed by double-loop stitching so as to extend over the links of the fastener element.

2. A slide fastener comprising a pair of interlocking fastener elements each made from a continuous filament and having a series of interconnected U-shaped links with a spacer element embraced therebetween, said fastener elements each being sewn on to respective supporting tapes and having a braided bead formed by double-loop stitching so as to extend over the links of the fastener element.

B. DePENNING
of DePENNING & DePENNING
Agent for the Applicant.

Dated this 28th day of December 1960.

Printed by The Nelys Printing Works, Calcutta-1.

T. Yoshida.
NO. 74720.

3 Sheets
Sheet 1.

Fig. 1

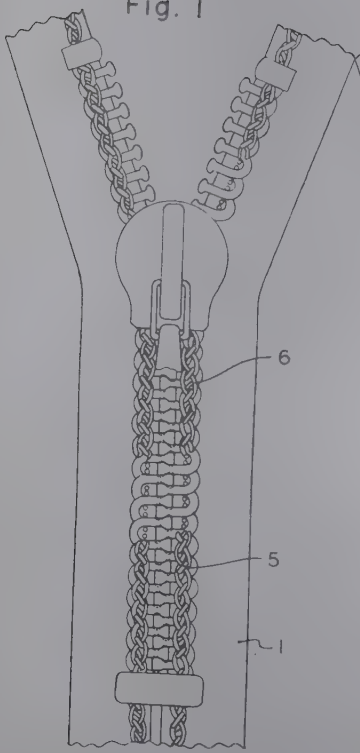


Fig. 2

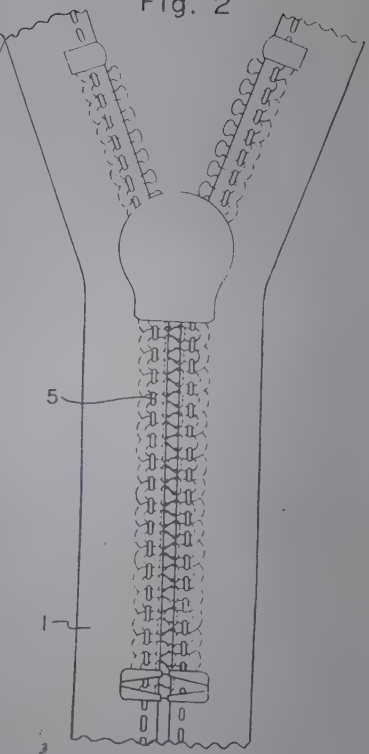
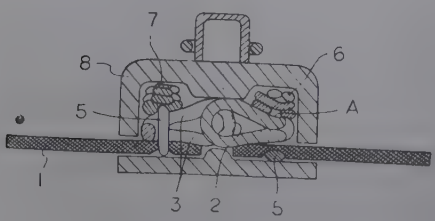


Fig. 3



B. Wilenning

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T. Yoshida.
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3 Sheets
Sheet 2.

Fig. 4

Fig. 5

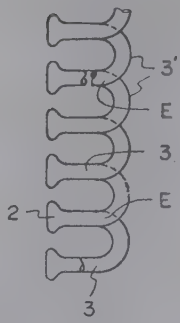

Fig. 9

Fig. 10

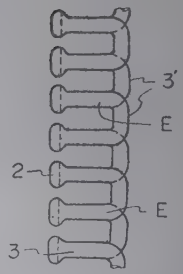

Fig. 6

Fig. 12

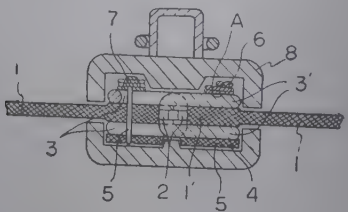

Fig. 11

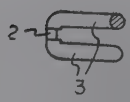

Fig. 13

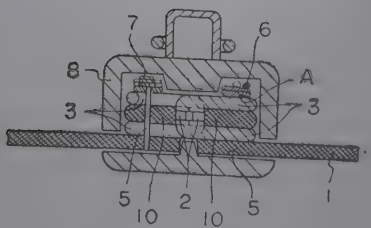

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Fig. 7

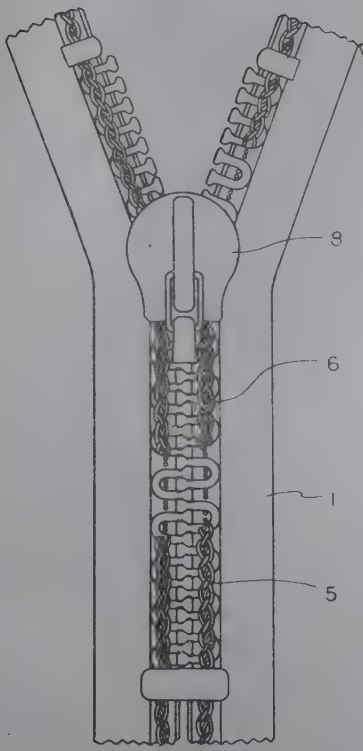


Fig. 8

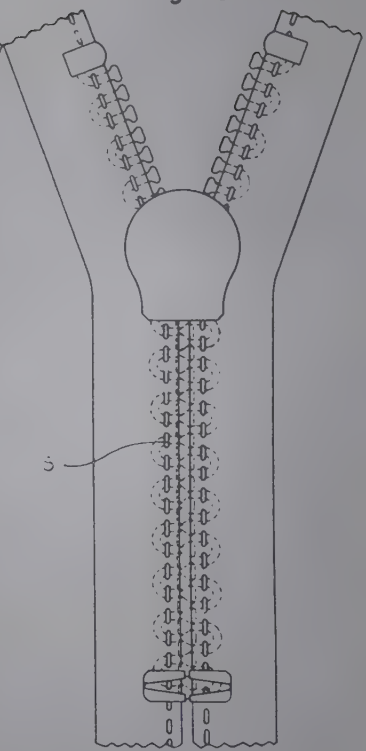
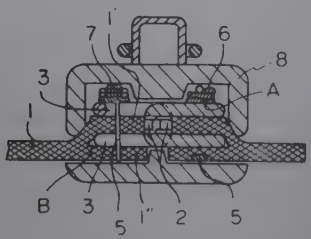


Fig. 14.



B DePenning

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Agent for the Applicant.

OF INSPECTION CENT

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74721, Application No. 74721 dated 28th December 1960. (Divided out No. 68811)
[Application and Provisional Specification ante-dated to 20th August 1959, under Section 5 of the I. P. & D. Act, 1911.] Complete specification left on 28th December 1960. [Complete specification ante-dated to 24th May 1960, under Section 5 of the I. P. & D. Act, 1911.]
(Application accepted 14th February 1961.)

PROVISIONAL SPECIFICATION.

"PHARMACEUTICAL PREPARATIONS CONTAINING NEW GUANIDINES"

CIBA LIMITED, CHEMICAL MANUFACTURERS, A SWISS CORPORATION, OF 141, KLYBECKSTRASSE, BASLE SWITZERLAND.

The following Specification describes the nature of this invention :—

The present invention concerns guanidine compounds. More particularly, it relates to (N, N-alkylene-imino)-lower alkyl-guanidines, in which the alkylene radical contains from four to nine carbon atoms as ring members, and in which at least one pair of two neighbouring carbon atoms of the alkylene radical are part of an aryl nucleus, and the salts thereof. Also anticipated are the acyl and quaternary ammonium derivatives thereof, as well as process for manufacturing such compounds.

The above-described N, N-alkylne-imino radical may be represented, for example, by N, N-tetramethylene-imino (1-pyrrolidino), N,N-pentamethylene-imino (1.piperidino), N, N-hexamethylene-imino (1-hexahydro-azopino), N, N-heptamethylene-imino (1-octahydro-azocino), N, N-octamethylene-imino (1-octahydro-azonino) or N, N-nonamethylene-imino (1-decahydro-azecino) radicals.

As previously stated, at least one pair of two neighbouring carbon atoms of the alkylene chain, are also incorporated into and form part of an aryl nucleus.

Such an aryl nucleus is above all a carbocyclic aryl nucleus, primarily a monocyclic carbocylic aryl, i. e. benzene, nucleus, or a bicyclic carbocylic aryl, e. g. a naphthyl [1, 2] or a naphthyl [2, 3] nucleus. The aryl nuclei may also be represented by heterocyclic aryl rings, such as monocyclic azacyclic aryl nuclei, particularly pyridine nuclei.

The above-described carbocyclic nuclei may contain additional groups, such as lower alkyl, e. g. methyl or ethyl, or functional groups, such as hydroxyl, etherified hydroxyl, particularly lower alkoxy, e. g. methoxy, ethoxy, n-propyloxy, isopropyloxy, or n-butyloxy, lower alkylenedioxy, e.g. methylenedioxy, or carbocyclic aryl-lower alkoxy, e.g. benzyloxy, esterified hydroxyl, such as lower alkoxy-carbonyloxy, e.g. methoxycarbonyloxy or ethoxycarbonyloxy, lower alkanoyloxy, e.g. acetoxy, or halogen, e.g. fluorine, chlorine or bromine, lower alkyl-mercapto, e.g. methyl-mercapto or alkyl-mercapto, lower alkanoyl, e.g. acetyl or propionyl, nitro amino, such as primary amino, secondary amino, particularly N-lower alkyl-amino, e.g. methylaminio or ethylamino, or primarily tertiary amino, such as N, N-di-lower alkyl-amino, e. g. dimethylamino, N-ethyl-N-methylamino or diethylamino, or N, N-lower alkylene-imino, N, N-lower oxa-alkylene-imino, or N, N-lower aza-alkylene-imino, in which radicals lower alkylene contains from four to six carbon atoms as ring members, e.g. pyrrolidino, piperidino, 2-methyl-piperidino, hexamethylene-imino, morpholino, 4-methyl-piperazino or 4-(2-hydroxy-ethyl)-piperazino, and the like, or halogeno-lower alkyl, e.g. trifluoromethyl, or analogous functional groups.

The N, N-alkylen-imino radicals in the (N,N-alkylene-imino)-lower alkyl-guanidine compounds of the present invention may be represented, for example, by 2-isoindolinyl, 1-indolinyl, 1-tetrahydroquinolyl, 2-tetrahydroisoquinolinyl, 1-N, N-benz [b]-hexamethylene-imino, 1-N, N-benz [d] hexamethylene-imino, 1-N, N-dibenz [b, f] hexamethylene-imino, 1-N, N-dibenz [e] heptamethylene-imino and the like, as well as benz-substituted derivatives of the abovementioned ring systems, whereby substituents are selected from the group of aforementioned groups and functional groups. The alkylene radical in the N, N-alkylene-imino portion is otherwise unsubstituted or may carry as additional substituents, lower alkyl, e. g. methyl or ethyl, groups.

The lower alkyl radical connecting the nitrogen atom of the N, N-alkylene-imino ring system with the guanidino group may be represented by lower alkylene radical, which may contain from one to five, preferably from two to three carbon atoms. Such lower alkylene radical may separate the ring system from the guanidino group, for example, by from one to five, advantageously by from two to three, carbon atoms. 1, 2-Ethylene, 1-methyl-1, 2-ethylene-1, 2-methylene 1,2-ethylene or 1, 3-propylene represent the preferred group of lower alkylene radicals, which may also include methylene, 1-methyl-1, 3-propylene, 1, 4-butylene, 1, 5-pentylene and the like.

The guanidino group is preferably unsubstituted. However, the amino as well as the imino groups of the guanidino portion may be substituted by lower hydrocarbon radicals, such as lower alkyl, e. g. methyl or ethyl; monomethyl-, polymethyl-, monoethyl-or polyethyl-substituted guanidino groups are anticipated.

Acyl derivatives of the new guanidine compounds of this invention are those formed with organic acids, particularly organic carboxylic acids, such as lower aliphatic carboxylic acids, for example, lower alkanoic acids, e. g. acetic, propionic or pivalic acid, substituted lower alkanoic acids, e. g. chloroacetic, dichloroacetic, hydroxyacetic, methoxyacetic, or cyclopenthyl-propionic acid, or lower alkenoic acids, e. g. acrylic acid, with carbocyclic aryl carboxylic acids, for example, monocylic carbocyclic aryl carboxylic acids, e. g. benzoic, hydroxy-benzoic or aminobenzoic acid, or bicyclic carbocylic aryl carboxylic acids, e.g. 1-naphthoic or 2-napthihoic acid, with carbocyclic aryl-lower aliphatic hydrocarbon carboxylic acids, such as monocyclic carbocylic aryl-lower alkanoic acids, e. g. phenylacetic or phenylpropionic acid, or with heterocoylic aryl carboxylic acids, for example, monocyclic heterocyclic aryl carboxylic acids, e.g. nicotinic, isonicotinic or 2-furoic acid.

Salts of the new compounds of this invention are paticularly therapeutically, acceptable, non-toxic acid addition salts, such as those with inorganic acids, for example, hydrohalic acids, e. g. hydrochloric or hydrobromic acid, sulfuric or phosphoric acids, or those with organic acids, such as acetic, propionic, glycolic, lactic, pyruvic, oxalic, malonic, succinic, maleic, fumaric, malic, tartaric, citric, ascorbic, hydroxy-maleic, dihydroxymaleic, benzoic, phenylacetic, 4-aminobenzoic, 4-hydroxybenzoic, anthranilic, cinnamic, mandelic, salicyclic, 4-aminosalicylic, 2-phenoxy-benzoic, 2-acetoxy-benzoic, methane sulfonic, ethene sulfonic, 2-hydroxyethane sulfonic and the like. Mono-or poly-salts may be formed.

The new guanidine compounds of this invention may also form quaternary ammonium compounds, particularly those with lower alkyl halides, e. g. methyl, ethyl, propyl or isopropyl chloride, bromide or iodide, as well as the corresponding quaternary ammonium hydroxides and the salts which may be formed from the quaternary ammonium hydroxides by the

reaction with inorganic acids other than the hydrohalic acids or with organic acids, such as those outlined above for the preparation of the acid addition salts.

The new guanidine compounds of the present invention may have antihypertensive properties, and may, therefore, serve as antihypertensive agents to relieve states of hypertension, such as those of benign or malignat character, or those associated with pregnancy, e. g. toxemia of pregnancy. These antihypertensive effects may be marked by long duration, which may be particularly useful in the treatment of chronic hypertensive conditions. The new guanidine compounds may also have other pharmacological properties, such as anticholinergic effects, which may be utilized in the treatment of spastic conditions, analgesic properties, which may counteract pain associated with chronic diseases or surgery, or, antihistaminic properties, which may counteract the effects of histamine, released in allergic disorders. They may also have antibacterial properties and may be used accordingly. Furthermore, they may serve as intermediates in the preparation of valuable compounds.

The new guanidine derivatives may be used as medicaments in the form of pharmaceutical preparations, which contain the new compounds or the salts thereof in admixture with a pharmaceutical organic or inorganic, solid or liquid carrier suitable for enteral or parenteral administration. For making up the preparations there can be empolyed substances which do not react with the new compounds, such as water, gelatine, lactose, starches, stearic acid, magnesium stearates, stearyl alcohol, talc. vegetable oils, benzyl alcohols, gums, propylene glycol, polyalkylene glycols, petroleum jelly or any other known carrier for medicaments. The pharmaceutical preparations may be in solid from, for example, as tablets, dragees or capsules, or in liquid form, for example, as solutions, suspensions or emulsions. If desired, they may contain auxiliary substances, such as preserving, stabilizing, wetting or emulsifying, agents, salts for varying the osmotic pressure or buffers and the like. They may also contain, in combination, other therapeutically useful substances.

The new guanidine compounds of this invention may be prepared by treating an N,N-alkylene-imino-lower alkyl-amine, in which the N, N-alkylene-imino group and the lower alkyl radical have the above-given meaning, or a salt thereof, with an S-lower alkyl-isothiourea or a salt thereof, and, if desired, converting a resulting salt into the free compound, and/or, converting a resulting compound into its acyl derivative, and/or if desired, converting a free compound into a salt or a quaternary ammonium compound thereof.

The isothiourea reagents used to form the guanidine derivatives of this invention are preferably employed in the form of their acid addition salts, particularly the salts with mineral acids, such as hydrohalic acids, e.g. hydrochloric or hydrobromic acid, or primarily with sulfuric acid. An S-lower alkyl radical is especially an S-ethyl, S-n-propyl, or particularly an S-methyl radical. The isothiourea reagent used in the reaction may be otherwise unsubstituted or the amino and/or imino groups of these reactants may be substituted by lower hydrocarbon radicals, such as lower alkyl, e.g. methyl or ethyl; such N-substituted isothiourea compounds provide for the formation of guanidine compounds, in which the amino and/or imino groups of the guanidino portion may be substituted. The preferred reagents to form a guanidino group are the S-methyl-isothiourea and the mineral acid addition salts thereof; S-methyl-isothiourea sulfate is primarily used to form guanidine compounds, which contain an unsubstituted guanidino group. In this procedure, the N, N-alkyleneimino-lower alkyl-amine used as the starting material, is preferably employed in the form of its free base.

The reaction is carried out by contacting the starting reagents with the reagent, preferably in the presence of a solvent, the choice of which is based primarily on the solubility of the reactants. Water or aqueous, alcoholic organic solvents, such as lower alkanols, e.g. methanol, ethanol, n-propanol, isopropanol or tertiary butanol, ethers, e. g. p-dioxane, ketones, e. g. acetone or ethyl methyl ketone, lower alkanoic acids, e. g. acetic acid, formamides, e. g. dimethyl-formamide, or aqueous mixtures of such solvents may be used as solvents. The reaction may be carried out at room temperature, or, if necessary, at an elevated temperature, for example, at the boiling temperature of the solvent. An absence of oxygen may be achieved by preforming the reaction in the atmosphere of an inert gas, e. g. nitrogen, and, if necessry, it may be carried out under pressure in a closed vessel.

Other reagents which may be used in an analogous manner are the O-lower alkyl-isoureas, in which lower alkyl represents primarily methyl or one of the abovementioned lower alkyl radicals, or the addition salts with mineral acids, particularly sulfuric acid. O-methyl-isourea sulfate is the reagent of choice, which, as well as other O-lower alkyl-isoureas or salts thereof, may be reacted with the N, N-alkylene-imino-lower alkyl-amine compound as previously shown for the S-lower alkyl-isothiourea reagents.

These isothiourea and the isourea derivatives are known, or, if now, may be prepared according to the methods used for the preparation of the known reagents. For example, S-lower alkyl-isothioureas or O-lower alkyl-isoureas may be prepared, for example, by alkylating thioureas or ureas, in which at least one of the nitrogen atoms, carries a hydrogen atom, with a lower alkyl halide, e.g. methyl or ethyl chloride, bromide or iodide or with a di-lower alkyl-sulfate, e.g. dimethyl sulfate or diethyl sulfate.

A second modification of the general procedure comprises reacting the N, N-alkylene-imino-lower alkyl-amine with a salt of a 1-guanyl-pyrazole derivative, for example, the nitrate of 1-guanyl-3,5-dimethyl-pyrazole. Although the reaction may proceed without the presence of a solvent, a lower alkanol, e.g. ethanol, may be used as a diluent. This modification is preferably carried out at an elevated temperature; in the absence of a solvent, the two reactants may be fused together at an elevated temperature.

The compounds of the present invention may also be obtained by reacting a salt of an N, N-alkylene-imino-lower alkyl-amine with cyanamide, if desired, in an aqueous or a lower alkanol, e. g. methanol or ethanol, solution, or by fusing the two reactants at an elevated temperature. Salts of the starting materials are primarily those with mineral acids, such as hydrohalic acids, or, primarily, sulfuric acid.

The N, N-alkyleneimino-lower alkyl-amines used as the starting materials in the above reaction may be prepared, for example, by treating N, N-alkylene-imines with halogeno-lower alkyl-nitriles, in which halogeno stands primarily for chlorine, or with lower alkene-nitriles, in which the double bond is activated by the nitrile group in such manner that it adds to the secondary amino group, and converting in the resulting N, N-alkylene-imino-lower alkyl-nitriles the nitrile group to a methylamino group by catalytic hydrogenation, such as, for example, by treatment with hydrogen in the presence of a catalyst containing a metal of the eighth group of the Periodic System, e. g. palladium on charcoal or Raney nickel, or, preferably, by treatment with a light metal hydride, for example, an alkali metal hydride, e. g. lithium aluminum hydride or sodium aluminum hydride, or other aluminum hydrides, e.g. magnesium aluminum hydride, aluminum borohydride or aluminum hydride, which hydrides may be used, if desired, in the presence of an activator, such as aluminum chloride.

Acyl derivatives of the guanidine compounds of the present invention may be prepared, for example, by treating a resulting guanidine compound with the reactive derivative of a carboxylic acid, for example, with a halide, e. g. chloride, or with the anhydride of a carboxylic acid. The reaction is preferably carried out in an inert solvent, for example, in a hydrocarbon, such as an aliphatic hydrocarbon, e.g. hexane, or an aromatic hydrocarbon, e.g. benzene, toluene or xylene, or in a tertiary organic base, such as a liquid pyridine compound, e. g. pyridine or collidine.

Depending on the conditions used, the new guanidine compounds may be obtained in the form of the free compounds or as the salts thereof. A salt may be converted into the free compound in the customary way, for example, by treatment with an aqueous alkaline reagent, such as an alkali metal hydroxide, e. g. lithium, sodium or potassium hydroxide, an alkali metal carbonate, e. g. lithium, sodium or potassium carbonate or hydrogen carbonate, or ammonia. A free base may be transformed into its therapeutically useful acid addition salts by reacting the former with an appropriate inorganic or organic acid, such as one of those outlined hereinabove, preferably in the presence of a solvent, such as a lower alkanol, e.g. methanol, ethanol, propanol or isopropanol, or an ether, e.g. diethylether or p-dioxane, and the like or in a mixture of solvents.

The guanidine compounds may be converted into the quaternary ammonium compounds by reacting the tertiary bases with an ester formed by a hydroxylated lower hydrocarbon compound with a strong inorganic or organic acid. Hydroxylated lower hydrocarbon compounds contain from one to seven carbon atoms and the esters thereof are more especially those with mineral acids, e. g. hydrochloric, hydrobromic, hydriodic, or sulfuric acid. Such esters are specifically lower alkyl halides, e. g. methyl, ethyl or n-propyl chloride, bromide or iodide, or lower alkyl lower alkane sulfonates, e. g. methyl or ethyl methane or ethane sulfonate. The quaternizing reaction may be performed in the presence or absence of a solvent, at room temperature or under cooling, at atmospheric pressure or in a closed vessel under pressure. Suitable solvents are more especially lower alkanols, e. g. methanol, ethanol, propanol, isopropanol, tertiary butanol or pentanol lower alkanones, e. g. acetone or ethyl methyl ketone, or organic acid amides, e. g. formamide or dimethylformamide.

The invention also comprises any modification of the general process wherein a compound obtainable as an intermediate at any state of the process is used as starting material and the remaining step (s) of the process is(are) carried out, as well as any new intermediates.

In the process of this invention such starting materials are preferably used which lead to final products mentioned in the beginning as preferred embodiments of the invention.

The following examples illustrate the invention and are not to be construed as being limitations thereon. Temperatures are given in degrees Centigrade.

Exmaple 1.

A mixture of 2.0 g. of 2-(1-N, N-benz [b] hexamethylene-imino)-ethylamine and 1.5 g. of S-methyl-isothiourea sulfate in a small amount of water is refluxed for four hours. The solution is concentrated and the 2-(1-N, N-benz [b] hexamethylene-imino)-ethyl-guanidine sulfate is recovered from the residue.

The starting material may be prepared as follows: 14.7 g. of N, N-benz [b] hexamethylene-imino and 7.6 g. of chloroacetonitrile are added to a suspension of 5.3 g. of anhydrous sodium carbonate in 75 ml. of benzene. The reaction mixture is vigorously stirred and refluxing is continued for an additional four hours. The reaction mixture is cooled, filtered, and the filtrate is evaporated to yield the 1-N, N-benz [b] hexamethylene-imino-acetonitrile. The latter is dissolved in dry diethyl ether and treated with lithium aluminum hydride while refluxing; the resulting 2-(1-N, N-benz [b] hexamethylene-imino)-ethylamine is obtained after evaporating the solvent.

Example 2.

A mixture of 2.0 g. of 2-(1-N, N-dibenz [b,f] hexamethylene-imino)- ethylamine and 1,2 g. of S-methyl-isothiourea sulfate in a small amount is refluxed for four hours; the desired 2-(1-N, N-dibenz [b, f] hexamethylene-imino)-ethyl-guanidine sulfate is obtained after concentrating the solution.

The starting material may be obtained according to the procedure of Example 1, i. e. by reacting 19.5 g. of 1-N, N-dibenz [b, f] hexamethylene-imine with 7.6 g. of chloroacetonitrile in the presence of a suspension of 5.3 g. of sodium carbonate in 75 ml. of benzene and reducing the resulting 1-N, N-dibenz [b,f] hexamethylene-imino)-ethylamine by treatment with lithium aluminum hydride.

Example 3.

A mixture of 1.5 g. of 2-(1-tetrahydroquinolyl)-ethylamine and 1. 2 g. of S-methyl-isothiourea sulfate in water yields the desired 2-(1-tetrahydroquinolyl)-ethyl-guanidine sulfate after refluxing for four hours and concentrating the solution.

The starting material may be obtained by refluxing a mixture of 13.3 g. of tetrahydroquinoline, 7.6 g. of chloroacetonitrile and 5.3 g. of anhydrous sodium carbonate in 75 ml. benzene and reducing the resulting 1-tetrahydroquinolyl-acetonitrile with lithium aluminum hydride in an ether solution.

Example 4

The 3-(2-isoindolinyl)-propyl-guanidine sulfate is obtained by refluxing a mixture of 2.0 g. of 3-(2-isoindolinyl)-propylamine and 1.8 g. of S-methyl-isothiourea sulfate in 7 ml. of water and concentrating the resulting solution.

The starting material may be obtained by adding 11.9 g. of isoindoline to 21.2 g. of acrylonitrile and a few drops of N-benzyl-N, N, N-trimethyl-ammonium hydroxide. After the initial reaction has subsided the mixture is refluxed for several hours, then cooled and the desired 2-isoindolinyl-propionitrile is recovered by fractionation. The 3-(2-isoindolinyl)-propyl-amine is obtained by reducing the 2-isoindolinyl-propionitrile with lithium aluminum hydride as shown in Example 1.

Other guanidine derivatives, which may be prepared according to the above described procedure are, for example, 2-(2-tetrahydroisoquinolyl)-ethyl-guanidine sulfate, 2-(4-methoxy-2-isoindolinyl)-ethyl-guanidine sulfate, 2-(1-N, N-(5-chloro-benz [b]) benz [f] hexamethylene-imino)-ethyl-guanidine sulfate; 2-(1-N, N-benz [b] hexamethylene-imino)-ethyl-guanidine sulfate, 2-(1-benz [b] heptamethylene-imino)-ethyl-guanidine sulfate and the like.

DePENNING & DePENNING,
Agents for the Applicants.

Dated this 28th day of December, 1960.

Printed by The Nelys Printing Works., Calcutta-1.

COMPLETE SPECIFICATION

Specification No. 74721, dated 28th December 1960.

"PHARMACEUTICAL PREPARATIONS CONTAINING NEW GUANIDINES."

CIBA LIMITED, Chemical Manufacturers, a Swiss Corporation, of 141, Klybeckstrasse, Basle, Switzerland.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

The present application is a division of our copending application No. 68811, filed August 20, 1959.

This invention relates to pharmaceutical preparation containing alkyleneimino-lower alkyl-guanidines in which the alkyleneimino group contains 4 to 9 ring carbon atoms and at least one fused-on isocyclic or heterocyclic aromatic nucleus, and in which the lower alkyl radical separates the imino from the guanido group by 1 to 5 carbon atoms, their acyl derivatives, quaternary ammonium compounds and their salts.

In the new compounds the guanido group is more especially unsubstituted ; it may, however, also be substituted, for example by aliphatic hydrocarbon radicals, advantageously lower alkyl groups, such as methyl, ethyl, n-propyl or isopropyl, and/or an acyl radical.

Aromatic nuclei fused-on to the alkyleneimino ring are more especially monocyclic radicals, for example benzene or pyridine rings, but also bicyclic radicals, such as linear or angular fused-on naphthalene or quinoline rings.

Examples of the above-described alkyleneimino radicals fused-on to aromatic nuclei are : indolinyl-(1), isoindolinyl-(2), tetrahydroquinolyl-(1), tetrahydroisoquinolyl-(2), 2:3-benzo-2:3-dehydro-hexyleneimino, 3:4-benzo-3:4-dehydro-hexyleneimino, 4:5-benzo-4:5-dehydro-hexyleneimino, 2:3-benzo-2:3 dehydro-heptyleneimino, 3:4-benzo-3:4-dehydro - heptyleneimino, 4:5-benzo-4:5-dehydro-heptyleneimino, 2:3; 6:7-dibenzo-2:3; 6:7-bis-dehydro-hexyleneimino or 3:4-naphtho-(2':3')-3:4-dehydro-heptyleneimino.

The above-mentioned ring systems are primarily unsubstituted in the non-aromatic portion, but they may also be substituted by hydrocarbon radicals, for exmple lower alkyl groups, such as methyl or ethyl groups. The aromatic portion may be substituted, for example, by the following groups : lower alkyl, such as methyl or ethyl, free, etherified or esterified hydroxyl, for example lower alkoxy, such as methoxy, ethoxy, n-propoxy or isopropoxy, lower alkylenedioxy, such as methylenedioxy, aralkoxy, such as benzyloxy, or lower alkoxy-carbonyloxy, such as methoxycarbonyloxy, lower alkanoyloxy, such as acetoxy or propionyloxy, halogen, such as fluorine, chlorine or bromine, or lower alkylmercapto, such as methyl-or ethyl-mercapto, lower alkanoyl, such as acetyl or propionyl, nitro, amino, mono-substituted amino, for example lower alkylamino, such as methyl or ethylamino, more especially disubstituted amino, for example di-lower alkylamino, such as dimethylamino, methyl-ethylamino, or diethylamino, or alkyleneimino in which the alkylene chain which may also be interrupted by oxygen or nitrogen atoms contains 4 to 6 ring carbon atoms, for example pyrrolidino, piperidino, 2-methyl-piperidino, hexamethyleneimino, morpholino, 4-methyl-piperazino or 4-β-hydroxyethyl-piperazino, or halogen-lower alkyl, such as trifluoromethyl.

In the new compounds the imino group is separated from the guanido group by 1 to 5, but preferably by 2 to 3, carbon atoms of the alkylene radical. The latter is particularly 1:2-ethylene, 1:2, 2:3, or 1:3-propylene, but also 1:2- or 1:4-butylene or 1:5-pentylene.

Acyl substituents of the guanido group are, for example, acyl radicals of lower aliphatic carboxylic acids, such as lower alkanecarboxylic acids, for example acetic, propionic or pivalic acid, or substituted lower alkanecarboxylic acids, such as chloracetic, dichloracetic, glycolic, methoxyacetic or β-cyclopentyl-propionic acid, or of lower alkene-carboxylic acids, such as acrylic acid, or of mono or bicyclic aromatic carboxylic acids, such as benzoic, para-hydroxy-benzoic, para-methoxy-benzoic, 3:4-dimethoxy-benzoic, 3:4:5-trimethoxy-benzoic, 4-0-ethoxy-carbonyl-syringic, 3:4-dichloro-benzoic, dimethylamino-benzoic, para-nitro-benzoic, 1-naphthoic or 2-naphthoic acid, or of mono-cyclic, heterocyclic carboxylic acids, such as nicotinic, isonicotinic acid or 2-furanecarboxylic acid.

Salts of the new compounds are more especially therapeutically useful acid addition salts, for example those of inorganic acids, such as hydrochloric acid, hydrobromic acid, sulfuric or phosphoric acids, or of organic acids, for example acetic, propionic, glycolic, lactic, pyruvic, oxalic, malonic, succinic, maleic, fumaric, malic, tartaric, citric, ascorbic, citraconic, hydroxymaleic or dihydroxymaleic acid, or benzoic, phenylacetic, 4-aminobenzoic, 4-hydroxybenzoic, anthranilic, cinnamic, mandelic, salicylic, 4-aminosalicylic, 2-phenoxy-benzoic or 2-acetoxy benzoic acid, or methane-sulphonic, ethane-sulphonic, 2-hydroxy-ethanesulphonic or paratoluene-sulphonic acid, mono- or poly-salts may be formed.

Quaternary ammonium compounds are primarily those which are formed by reaction with reactive esters of lower alkanols or aralkanols. From these addition products the ammonium hydroxides may be obtained which may be reacted with the above-mentioned therapeutically useful acids to form other quaternary ammonium salts.

The new preparations inhibit the hypertensive i.e. blood pressure increasing, effect of 1-phenyl-2-amino-propane (amphetamine) or similar sympathomimetic drugs without affecting their stimulating properties. They can therefore be used, for example, in combination with sympathomimetic drugs of the amphetamine type to offset the hypertensive side effects of such drugs without affecting their very valuable stimulating effect.

In addition, the new preparation have antihypertensive properties and bring about an increase in peripheral blood flow. They can consequently be used as agents in cases of high blood pressure, especially neurogenic, renal or essential hypertension, and in the treatment of peripheral vascular diseases, for example Raynaud's disease. The effects produced by the new preparations last relatively long which makes them especially suitable for the treatment of chronic forms of hypertension.

A preferred group of the new preparations are such as contain compounds of the formula shown in figs. 1 and 2 of the drawings accompanying this specification, in which R_1 and R_1 stand for hydrogen, alkyl or alkoxy containing 1 to 4 carbon atoms, or halogen with an atomic weight of below 80, each of the symbols n_1 and n_2 stands for one of the numbers 0 to 5, with the proviso that the total of $n_1 + n_2$ represents one of the numbers 2, 3, 4 or 5, each of the symbols m_1, m_2 and m_3 represents one of the numbers 0, 1 or 2, with proviso that the total of $m_1 + m_2 + m_3$ represents one of the numbers 0 to 4, and A represents an alkylene radical containing 2 to 3 carbon atoms and separating the guanido group from the imino group by at least 2 carbon atoms, and their acid addition salts.

Particularly valuable are preparations containing compounds of the formula shown in fig. 3 of the said drawings, in which n_3 represents one of the numbers 2, 3 or 4, especially 2-[1:2:3:4-tetrahydro-isoquinolyl-(2)]-ethyl-guanidine of the formula shown in fig. 4 of the said drawings, and their acid addition salts, particularly those with therapeutically useful mineral acids, especially sulphuric acid.

Other valuable preparations are those which contain one of the following compounds: 2-(2:3 benzo-2:3-dehydrohexyleneimino)-ethyl-guanidine, 2-(2:3;6:7-dibenzo-2:3;6:7-bis-dehydrohexyleneimino)-ethyl-guanidine, 2-[1:2:3:4-tetrahydro-quinolyl-(1)]-ethyl-guanidine, 2-[7-chloro-1:2:3:4-tetrahydro-quinolyl-(1)]-ethyl-guanidine, 3-[1:2:3:4-tetrahydroquinolyl-(1)]-propylguanidine, 3-[isoindolinyl-(2)]-propyl guanidine, 2-[isoindolinyl-(2)]-ethyl-guanidine, 2-[4-methyl-isoindolinyl-(2)]-ethyl-guanidine, 2-(4:5-benzo-4:5-dehydrohexyleneimino)-ethyl-guanidine, 2-(2 : 3-benzo-2:3-dehydro-heptyleneimino)-ethyl-gunnidine, 3-[1:2:3:4-tetrahydro-isoquinolyl-(2)]-propyl-guanidine, 2-[6-methoxy-1:2:3:4-tetrahydro-isoquinolyl-(2)]-ethyl-guanidine, 2-[6:7-dimethoxy-1:2:3:4-tetrahydro-isoquinolyl-(2)]-ethyl-guanidine, 2-[7-chloro-1:2:3:4-tetrahydro-isoquinolyl-(2)]-ethyl-guanidine, 1-[2-[1:2:3:4-tetrahydro-isoquinolyl-(2)]-ethyl}-3-methyl-guanidine or 1-[2-[1:2:3:4-tetrahydro-isoquinolyl-(2)]-ethyl}-3-benzoyl-guanidine and their therapeutically useful acid addition salts, particularly mineral acid addition salts, for example the sulphates.

The new preparations can be prepared by conventional methods from the above mentioned new guanidines, their salts, acyl derivaties and quaternary ammonium compounds which are the active substances. These preparations contain the active substances in admixture with a pharmaceutical organic or inorganic, solid or liquid carrier suitable for enteral, for example oral, or parenteral administration. For making up the preparations such substances can be employed as do not react with the active substances, for example, water, gelatine, lactose, starches, magnesium stearate, talc, vegetable oils, benzyl alcohols, gums, polyalkylene glycols, white petroleum jelly, cholesterol or any other known carrier for medicaments. The pharmaceutical preparations may be in the form of tablets, dragees or capsules or in liquid form as solutions, suspensions or emulsions. If desired, they may be sterilized and/or contain auxiliary substances, such as preserving, stabilizing, wetting or emulsifying agents, salts for varying the osmotic pressure or buffers. They may also contain other therapeutically useful substances.

The new pharmaceutical preparations, preferably tablets, dragees or capsules, may contain from about 0.1 to about 60% preferably from 0.1 to 30%, but especially from 5 to 15% of the active substance. In the case of solutions for parenteral administration, for example solutions for injection, the content of the active ingredient is between 0.1%, and 10%, preferably between 0.1% and 2.5%.

The alkyleneimino-lower alkyl-guanidines used in the manufacture of the new preparations are obtained according to the process of Indian Specification No. 68811 by converting in a manner known *per se* an alkyleneimino-lower alkyl-amine or a reactive functional derivative of N (alkyleneimino-lower alkyl)-carbamic acids which is convertible into a guanidine, or a salt thereof, into a corresponding guanidine; or in an alkyleneimino-lower alkyl-guanidine in which one carbon atom of the lower alkyl group and/or one or two ring carbon atoms of the alkyleneimino radical with a vicinal imino and/or guanido nitrogen atom form a carbamyl or thiocarbamyl grouping, or in a salt thereof, converting in conventional manner the carbonyl or thiocarbonyl groups into methylene groups; or in a reactive guanido-lower alkanol ester or alkyleneimino-lower alkanol ester or a salt thereof exchanging in a manner known *per se* the ester group for the alkyleneimino or a guanido group respectively; in the above compounds the alkyleneimino group contains 4 to 9 ring carbon atoms and at least one fused-on isocyclic or heterocyclic aromatic nucleus and in which the lower alkyl, alkanoyl or alkanol radical separates the imino group from the amino or the ester group by 1 to 5 carbon atoms; and, if desired, acylating the resulting compounds by a method known *per se* and/or converting them by known methods into quaternary ammonium compounds and/or converting in conventional manner resulting salts into the free compounds or resulting free compounds into their salts.

The following Example illustrates the invention:

Example

Capsules with a content of 25 mg of 2-[1:2:3:4-tetrahydro-isoquinolyl-(2)]-ethyl-guanidine sulphate can be prepared as follows:

Ingredients for 1000 capsules:	
2-[1:2:3:4-tetrahydro-isoquinolyl-(2)]-ethyl-guanidine sulphate	25 g
lactose	245 g
talc	30 g

The above ingredients are mixed until homogeneity is obtained. 300 mg portions of the mixture then filled into hard gelatine capsules.

In an analogous manner capsules may be prepared containing up to 100 mg of the active substance for the treatment of hypertension.

The 2-[1:2:3:4-tetrahydro-isoquinonyl-(2)]-ethyl-guanidine sulphate used as the active ingredient can be obtained as follows:

A homogeneous mixture of 9.1 grams of 2-[1:2:3:4-tetrahydro-isoquinolyl-(2)]-ethylamine, 7.2 grams of S-methyl-isothiourea sulphate and 9 cc of water is refluxed for six hours until the evolution of methyl-mercaptan ceases.

A precipitate is formed on standing overnight which is filtered off and recrystallized from anhydrous ethanol to yield 2-[1:2:3:4-tetrahydro-isoquinolyl-(2)]-ethyl-guanidine of the formula shown in fig. 4 of the said drawings, in the form of its sulphate melting at 204-207°C. The salt contains 2 mols of the base per one mol of sulphuric acid and half a mol of water of crystalization.

The starting material may be obtained as follows:

A mixture of 30.6 grams of 1:2:3:4-tetrahydro-isoquinoline, 17.3 grams of chloracetonitrile, 95.2 grams of anhydrous potassium carbonate and 200 cc of toluene is kept at the boil for 4 1/2 hours with stirring. After cooling, the reaction mixture is filtered, the solvent evaporated under reduced pressure and the residue distilled to yield 1:2:3:4-tetrahydro-isoquinolyl-(2)-acetonitrile boiling at 170-190°C under 24 mm of pressure.

To a solution of 23.3 grams of the resulting nitrile in 100 cc of diethyl ether a mixture of 6.1 grams of lithium aluminium hydride in 150 cc of ether is added in the course of half an hour with stirring at room temperature, and stirring is continued for 2 hours at room temperature. The reaction mixture is then treated successively with 18.5 cc of ethyl acetate, 6.3 cc of water, 12.3 cc of aqueous sodium hydroxide solution of 15% strength and 18.5 cc of water, and the organic phase is separated. After evaporating the ether, there is obtained by distillation 2-[1:2:3:4-tetrahydro-isoquinolyl-(2)]-ethylamine boiling at 82.88°C under 0.1 mm of pressure.

We Claim:-

1. Pharmaceutical preparations containing 0.1 to 60% of alkylene-imino-lower alkyl-guanidines in which the alkyleneimino group contains 4 to 9 ring carbon atoms and at least one fused-on isocyclic or heterocyclic aromatic nucleus and in which the lower alkyl radical separates the imino group from the guanido group by 1 to 5 carbon atoms, their acyl derivatives, quaternary ammonium compounds and their salts in admixture with a suitable carrier.

2. Pharmaceutical preparations containing alkylene-imino-lower alkyl-guanidines in which the alkylene-imino group contains 4 to 9 ring carbon atoms and at least one fused-on isocyclic or heterocyclic aromatic nucleus and in which the lower alkyl radical separates the imino group from the guanido group by 1 to 5 carbon atoms, their acyl derivatives, quaternary ammonium compounds and their salts in admixture with a suitable solid carrier.

3. Pharmaceutical preparations containing 0.1 to 60% of the active substances mentioned in claim 1 in admixture with a suitable liquid carrier.

4. Pharmacoutical preparations for injection containing 0.1 to 60% of the active substances mentioned in claim 1 in admixture with a carrier suitable for injection.

5. Pharmaceutical preparations in tablet form containing the active substances mentioned in claim 2 in admixture with a suitable solid carrier.

6. Pharmaceutical preparations in capsules form containing the active substances mentioned in claim 2 in admixture with a suitable solid carrier.

7. Pharmaceutical preparations as claimed in claims 2,5 and 6 said preparations containing 0.1 to 60% of the active substance.

8. Pharamaceutical preparations as claimed in claims 1 to 6 said preparations containing 0.1 to 30% of the active substance.

9. Pharamaceutical preparations as claimed in claims 1 to 6 said preparations containing 5 to 15% of the active substance.

10. Pharmaceutical preparations as claimed in claims 1, 3 and 4, said preparations containing 0.1 to 10% of the active substance.

11. Pharmaceutical preparations as claimed in claims 1, 3, 4 and 10, said preparations containing 0.1 to 2.5% of the active substance.

DePENNING & DePENNING

Agents for the Applicants.

Dated this 28th day of December 1960.

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Complete Specification.

One Sheet.

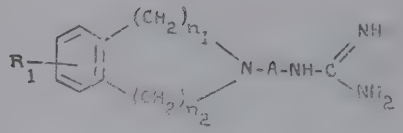

FIG. 1

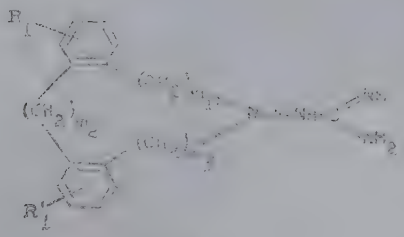

FIG. 2

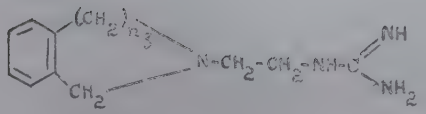

FIG. 3

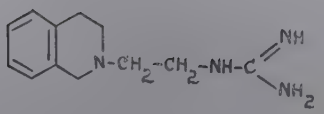

FIG. 4

B. DePenning

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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74722. Application No. 74722, dated 28th December 1960. (Divided out of No. 69382.) [Application and Provisional Specificaton anti-dated to 19th October 1959, under Section 5 of the I. P. & D. Act 1911.] Complete Specification left on 28th December 1960. [Complete Specification anti-dated to 8th August 1960, under Section 5 of the Act 1911.] (Application accepted 12th July 1961.)

PROVISIONAL SPECIFICATION.

PHARMACEUTICAL PREPARATIONS CONTAINING NEW 18-0-METHYLRESERPIC ACID METHYL EASTER.

CIBA LIMITED, CHEMICAL MANUFACTURERS, A SWISS CORPORATION, OF 141, KLYBECKSTRASSE, BASLE, SWITZERLAND.

The following specification describes the nature of this invention.

The present invention concerns ethers of deserpidates. More particularly, it relates to 18-0-ethers of deserpidates having the formula shown in Fig. 1 of the accompanying drawings, in which R_1 represents lower alkyl, lower alkoxy-lower alkyl or tertiary amino-lower alkyl, R_2 stands for lower alkyl, R_3 represents a lower aliphatic hydrocarbon or a substituted lower aliphatic hydrocarbon radical, R_4 stands for hydrogen lower alkyl, lower alkoxy, monocyclic carbocyclic aryl-lower alkoxy, lower alkyl-mercapto or halogen, each of the substituents R_5, R_6 and R_7 represents primarily hydrogen, on one of the substituents characteristic of R_4, whereby two neighbouring substituents, when taken together, may also form a lower alkylenedioxy radical, and each of the radicals R'_3 and R''_3 represents hydrogen or lower alkyl, and salts thereof, and process for the preparation of such compounds.

A lower alkyl group R_1 stands, for example, for methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, isopentyl, n-hexyl and the like.

In a lower alkoxy-lower alkyl group R_1, the lower alkoxy portion may be, for example, methoxy, ethoxy, n-propyloxy, iso propyloxy and the like. The tertiary amino group of a tertiary amino-lower alkyl radical R_1 is primarily an N,N-di-lower alkyl-amino group, in which lower alkyl contains from one to four carbon atoms, *e.g.*, dimethylamino, diethylamino, di-n-propylamino or di-isopropylamino and the like, an N,N-lower alkylene-imino group, in which lower alkylene contains from four to six carbon atoms, *e.g.*, pyrrolidino, piperidino or hexamethyleneimino, an N,N-lower oxa-alkylene-imino group, in which lower oxa-alkylene contains, preferably, four carbon atoms, *e.g.*, morpholino, or an N,N-lower aza-alkylene-imino group, in which lower aza-alkylene contains, preferably, four carbon atoms, *e.g.*, N-methyl-piperazino.

The lower alkyl portion of a lower alkoxy-lower alkyl radical R_1 or a tertiary amino-lower alkyl radical R_1 is represented by a lower alkylene radical, which separates the lower alkoxy group or the tertiary amino group from the carboxyl portion of the carboxyl group by at least two, preferably by two to three, carbon atoms. Such radicals are primarily 1,2-ethylene, 1-methyl-1,2 ethylene or 2-methyl-1,2-ethylene or 1,3-propylene ; other lower alkylene radicals may be 1,4-butylene or 1-methyl-1,3-propylene and the like.

The lower alkyl group R_2 may stand for ethyl, propyl, isopropyl, but represents above all methyl.

Generally, R_3 represents a lower aliphatic hydrocarbon or a substituted lower aliphatic hydrocarbon radical ; substituted lower aliphatic hydrocarbon radicals may contain as functional groups lower alkoxy, tertiary amino and the like. R_3 represents, primarily, lower alkyl, such as, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, isopentyl or nehexyl and the like. These radicals may contain as functional groups lower alkoxy, *e.g.*, methoxy or ethoxy and the like, tertiary amino-lower alkyl, such as N,N-di-lower alkyl-amino, *e.g.*, N,N-dimethylamino, N-ethyl-N-methyl-amino, N,N-diethylamino and the like, N,N-lower alkylene-imino, in which alkylene contains, primarily, from four to six carbon atoms, *e.g.*, pyrrolidino, piperidino, hexamethyleneimino and the like, N,N-lower oxa-alkylene-imino, in which alkylene contains, primarily, four carbon atoms, *e.g.*, morpholino, N,N-lower aza-alkylene-imino, in which alkylene contains, primarily, four carbon atoms, *e.g.*, 4-methylpiperazino and the like. Preferably, these substituents are separated from the oxygen atom of the 18-position of the deserpidate nucleus by at least two, advantageously, by two to three, carbon atoms. Substituted lower aliphatic hydrocarbon radicals, representing R_3, are, therefore, 2-lower alkoxy-ethyl, *e.g.*, 2-methoxy-ethyl or 2-ethoxyethyl, 3-lower alkoxy-propyl, *e.g.*, 3-methoxy-propyl, 2-N,N-di-lower alkylamino-ethyl, *e.g.*, 2-dimethylaminoethyl or 2-diethylaminoethyl, 3-N,N-di-lower alkyl-amino-propyl, *e.g.*, 3-dimethylaminopropyl, or 2-N,N-lower alkylene-imino-ethyl, *e.g.*, 2-(1-piperidino)-ethyl, or 3-N,N-lower alkylene-iminopropyl, *e.g.*, 3-(1-pyrrolidino)-propyl, and the like

The substituent R_4 represents primarily hydrogen or lower alkoxy, *e.g.*, ethoxy, n-propyloxy, isopropyloxy, or particularly methoxy. It may also stand for monocyclic carbocyclic aryl-lower alkoxy, *e.g.*, benzyloxy, lower alkylmercapto, *e.g.*, methylmercapto or ethylmercapto, lower alkyl, *e.g.*, methyl or ethyl, or halogen, *e.g.*, fluorine, chlorine or bromine. The substituents R_5, R_6 and R_7 represent primarily hydrogen ; they may also stand for the substituents characteristic for R_4, such as, for example lower alkyl, *e.g.*, methyl or ethyl, lower alkoxy, *e.g.*, methoxy or ethoxy, or halogen, *e.g.*, chlorine or bromine. Furthermore, two neighbouring substituents selected from R_4, R_5, R_6 and R_7, when taken together, may form a lower alkylenedioxy, *e.g.*, methylenedioxy, radical

Each of the radicals R'_3 and R''_3 stands, preferably, for hydrogen ; when representing lower alkyl, such radical may stand for ethyl, or primarily for methyl.

Salts of the new compounds of this invention are pharmaceutically acceptable addition salts with acids, primarily with inorganic acids, such as mineral acids. *e.g.*, hydrochloric, hydrobromic, sulfuric or phosphoric acid and the like, or with strong, organic acids, *e.g.*, acetic, hydroxyacetic or methane sulfonic acid and the like.

The new compounds of this invention have sedative and tranquilizing effects on the central nervous system ; they may also exhibit antihypertensive properties. Furthermore, tests show that animals, treated with the compounds of the present invention, recover faster and more completely from the pharmacological effects than those treated with known, naturally occurring Rauwolfia alkaloids, such as reserpine, deserpidine or rescinnamine. In addition, certain quantitative differentiations may be observed within the group of the new compounds of this invention. Thus, when compared with the established ratio existing between anti-hypertensive and sedative effects in the above-mentioned natural Rauwolfia alkaloids, some of the compounds of this invention have more predominant sedative effects with negligible antihypertensive activity, whereas in others, the latter effect may be more pronounced than the sedative and tranquilizing component.

The compounds of the present invention may, primarily, be used as sedative agents to relieve states of hyperactivity, tension and agitation as, for example, associated with mental disturbances. Compounds with a predominating antihypertensive effect may also be employed as antihypertensive agents to relieve hypertensive conditions as, for example, benign or malignant hypertension, renal hypertension or hypertension associated with pregnancy, such as toxemia of pregnancy.

The above-described properties are particularly exhibited by lower alkyl, 2-lower alkoxy-ethyl or 2-N,N-di-lower alkyl-amino-ethyl 11-R-18-0-R_3-deserpidates, in which R_3 stands for lower alkyl, especially methyl, and R_4 for hydrogen or methoxy. Representing this group of compounds are lower alkyl, *e.g.*, methyl, ethyl, n-propyl or n-butyl, 18-0-methyl-deserpidate or lower alkyl, *e.g.*, methyl, ethyl, n-propyl or n-butyl, 18 0-methyl-reserpate, lower alkoxy-lower alkyl, *e.g.*, 2-methoxyethyl, 18-0-methyl-deserpidate, lower alkoxy-lower alkyl, *e.g.*, 2-methoxyethyl, 18-0-methyl-reserpate, N,N-di-lower alkyl-amino-lower alkyl, *e.g.*, 2-dimethylaminoethyl, 18-0-methyl-deserpidate or N,N-di-lower alkyl-amino-lower alkyl, *e.g.*, 2-dimethylaminoethyl, 18-0-methyl-reserpate, as well as the corresponding 18-0-ethyl, 18-0-n-propyl, 18-0-n-butyl, 18-0-isobutyl, 18-0-n-pentyl analogs thereof and the like. Other 18-0-lower alkyl-deserpidates, especially 18-0-methyl-derivatives, are those of lower alkyl, *e.g.*, methyl ethyl, n-propyl or n-butyl and the like, 2-lower alkoxy-ethyl, *e.g.*, 2-methoxy-ethyl, or 2-N,N-di-lower alkyl-amino-ethyl, *e.g.*, 2-N,N-dimethylaminoethyl, esters of 9-methyl-deserpidic acid, 11-methyl-deserpidic acid, 9-methoxy-deserpidic acid, 10-methoxy-deserpidic acid, 10-methoxy-reserpic acid, 11-ethoxy-

deserpidic acid, 11-n-propyloxy-deserpidic acid, 11-isopropyloxy-deserpidic acid, 11-n-butyloxy-deserpidic acid, 10,11-methylenedioxy-deserpidic acid, 10-benzyloxy-deserpidic acid, 11-benzyloxy-deserpidic acid, 11-methylmercapto-deserpidic acid, 11-ethylmercapto-deserpidic acid, 10-chloro-deserpidic acid 5-methyl-reserpic acid, 6-methyl-deserpidic acid, 6-methyl-reserpic acid, 17-desmethoxy-17-ethoxy-reserpic acid, 17-desmethoxy-17-n-propyloxy-reserpic acid or 17-desmethoxy-17-isopropyloxy-reserpic acid and the like.

The compound of this invention may be used as medicaments in the form of pharmaceutical preparations, which contain the new compounds or salts thereof in admixture with a pharmaceutical organic or inorganic, solid or liquid carrier suitable for enteral, *e.g.*, oral, or parenteral administration. For making up the preparations there can be employed substances which do not react with the new compounds, such as water, gelatine, lactose, starches, stearic acid, magnesium stearate, stearyl alcohol, talc, vegetable oils, benzyl alcohols, gums, waxes, propylene glycol, polyalkylene glycols or any other known carrier for medicaments. The pharmaceutical preparation may be in solid form, for example, as solutions, suspensions or emulsions. If desired, they may contain auxiliary substances such as preserving agents, stabilizing agents, wetting or emulsifying agents, salts for varying the osmotic pressure or buffers. They may also contain, in combination, other therapeutically useful substances.

The 18-O-R_3-derivatives of lower alkyl, lower alkoxy-lower alkyl or tertiary amino-lower alkyl deserpidates, in which R_3 represents hydrocarbon, paticularly lower alkyl, may be formed by reacting a compound of the formula shown in Fig. 2 of the drawings in which R_1, R_2, R_4, R_5, R_6, R_7, R's and R"s have the above-given meaning, or a salt thereof, with a lower aliphatic diazo-hydrocarbon or a substituted lower aliphatic diazo-hydrocarbon derivative in the presence of a strong inorganic Lewis acid, and if desired, converting a resulting salt into the free base, and/or, if desired, converting a free base into a salt thereof.

Salts of the deserpidates used as the starting materials are addition salts with acids, primarily those with inorganic acids. Advantageously, those with the strong inorganic Lewis acids, catalyzing the etherification reaction, *e.g.*, fluoboric acid, are used; they may also be formed *in situ* upon addition of the Lewis acid to the reaction mixture.

The lower alkyl, lower alkoxy-lower alky or tertiary amino-lower alkyl deserpidates or salts thereof are reacted with the diazo compound, *e.g.*, lower diazo-alkane, lower alkoxy-lower diazo-alkane or tertiary amino-lower diazo-alkane, in the presence of a strong inorganic Lewis acid. Preferred Lewis acids contain (if desired, apart from others) the elements fluorine and/or boron; they are represented, for example, by fluoboric acid, which may be used in the form of a concentrated aqueous solution (for example, a 12 N to 16 N solution) or boron trifluoride, for example, in the form of its etherate with diethyl ether. In view of the salt-forming properties of the deserpidic acid ester, the Lewis acid, which catalyzes the etherification of the 18-hydroxyl group, is used in excess of the mole; an about one to about two hundred, preferably an about ten to about fifty, per cent. excess appears to be sufficient to promote the etherification reaction.

The reaction is carried out according to standard etherification procedures; solvents are preferably inert towards the reaction reagents and are represented, for example, by halogenated lower aliphatic hydrocarbons, *e.g.*, methylene chloride, ethers, *e.g.*, diethylether or tetrahydrofuran, or more polar solvents, such as, for example, lower alkyl lower alkanoates, *e.g.*, ethyl acetate, or acetonitrile and the like, as well as mixtures of such solvents. A solution of the diazo reagent in an inert solvent, such as an ether, *e.g.*, diethylether or a halogenated hydrocarbon, *e.g.*, methylene chloride, or a mixture thereof, may be added to the mixture of a deserpidic acid ester and a Lewis acid, preferably kept in solution. The diazo compound may also be distilled out of its solution into the solution of the mixture of the deserpidic acid ester and the Lewis acid. Furthermore, the mixture may also be given to the solution of the diazo reagent.

The reaction may be carried out at room temperature, however, cooling of the reaction mixture to below room temperature, for example, to from about 10° to about —20°, especially to from about 0° to about —15°, may be advantageous. If necessary, the reaction may be carried out in the atmosphere of an inert gas, *e.g.*, nitrogen.

An excess of the diazo reagent present at the end of the reaction may be destroyed, for example, by adding an acid, preferably an esterifiable carboxylic acid, *e.g.*, acetic or benzoic acid.

The desired product may be isolated according to standard procedures, *e.g.*, extraction, adsorption and elution, crystallization, etc. and purified, for example, by recrystallization, if necessary, after treatment of a solution thereof with an adsorbent, *e.g.*, aluminum oxide, charcoal, diatomaceous earth and the like.

The lower alkyl, lower alkoxy-lower alkyl or tertiary amino-lower alkyl deserpidates used as the starting materials are known or, if new, may be prepared according to procedures used for known analogs. For example, deserpidic acids may be esterified by treatment with a lower diazo-alkane, a lower alkoxy-lower diazo-alkane or a tertiary amino-lower diazo-alkane, or by alcoholysis of deserpidic acid (16,17→18)-lactones with alkali metal compounds of lower alkanols, lower alkoxy-lower alkanols or tertiary amino-lower alkanols.

Thus, to a solution of the diazo reagent in an inert solvent, such as an ether, particularly diethylether, may be added a free deserpidic acid compound, which is preferably kept in a suspension or a solution, for example, with a lower alkanol, *e.g.*, methanol or ethanol, or a halogenated aliphatic hydrocarbon, *e.g.*, chloroform. Or, the diazo compound may be distilled out of a solution, such as a diethylether solution, into the suspension or solution of a deserpidic acid. An excess of the diazo derivative present in the reaction mixture may be destroyed, for example, by adding an additional carboxylic acid, *e.g.*, acetic or benzoic acid. The esterification may be carried out under cooling or at room temperature, and, if desired, under the atmosphere of an inert gas, *e.g.*, nitrogen.

Or, by treating the necessary amount of an alkali metal, *e.g.*, lithium, potassium, or particularly sodium, with a lower alkanol, a lower alkoxy-lower alkanol or a tertiary amino-lower alkanol and adding a deserpidic acid lactone to the resulting alkali metal derivative of the alcohol, the desired deserpidate may be obtained. Although this reaction may proceed under cooling or at room temperature, the mixture is advantageously heated, if necessary, in the atmosphere of an inert gas, *e.g.*, nitrogen.

The compounds of this invention are obtained in the form of the free bases or the salts thereof. A salt may be converted into the free base, for example, by reaction with an aqueous basic reagent, such as, for example, aqueous ammonia. A free base may be converted into its therapeutically useful acid addition salts by reaction with one of the inorganic or organic acids outlined hereinbefore, for example, by treating a solution of the base in a lower alkanol, *e.g.*, methanol, or in a lower alkyl lower alkanoate, *e.g.*, ethyl acetate, with the acid or a solution thereof. Mono- or poly-salts may be formed, depending on the number of salt-forming groups and/or the conditions of salt formation.

The invention also comprises any modification of the process wherein a compound obtainable as an intermediate at any stage of the process is used as starting material and the remaining step(s) of the process is (are) carried out, as well as any new intermediates.

In the process of this invention such starting materials are preferably used which lead to final products mentioned in the beginning as preferred embodiments of the invention.

The following examples will serve to illustrate the invention; they are not to be construed as being limitations thereon. Temperatures are given in degrees Centigrade.

Example 1.

To a solution of 2·48 g. of methyl reserpate in 400 ml. of methylene chloride, maintained at —10 to —15°, is added 56 ml. of fluoboric acid solution while stirring. (The latter is prepared as follows: Commercially available fifty per cent. aqueous fluoboric acid is concentrated by partial evaporation under reduced pressure to an approximately 14 N solution, determined by titration with a standard sodium hydroxide solution. A stock solution of approximately 0·1 N strength is prepared by dissolving 1 ml. of the concentrated fluoboric acid in a mixture of 110 ml. of absolute ether and 30 ml. of methylene cholride). A small precipitate forms during the addition, which represents, probably, a salt of methyl reserpate with the acid.

A solution of diazomethane in methylene chloride (69 ml. of a 0·348 N solution) is added to the stirred reaction mixture

over a period of about five minutes whereby the temperature is maintained at —10°. The previously-mentioned precipitate dissolves again. An additional 1 ml. of the stock solution of fluoboric acid is given to the reaction mixture, and the solution is stirred for a few more minutes. 2 ml. of glacial acetic acid is added with the intent to destroy any excess of diazomethane.

The solution is washed twice with five per cent. aqueous sodium carbonate and once with saturated aqueous sodium chloride, the organic layer is dried over anhydrous sodium sulfate and evaporated under reduced pressure, whereupon 2·24 g. of a tan, solid material can be recovered. As much as possible of the residue is dissolved in 50-60 ml. of benzene at room temperature ; the undissolved material, representing methyl reserpate, is filtered off. The filtrate is chromatographed on about 40 g. of aluminum oxide (Woelm, neutral, activity I); the desired methyl 18-0-methyl-reserpate is eluted with benzene, containing 0·2 per cent. of methanol. The oily, yellow solid is washed with cold ether and recrystallized from a 1:3-mixture of benzene and cyclohexane, using charcoal as a decolorizing agent, m.p. 228-231° (with decomposition).

Example 2.

Substitution of the diazomethane solution in Example 1 by 113 ml. of a 0·212 N solution of diazoethane, adding said solution to the mixture of methyl reserpate and fluoboric acid over a period of ten minutes and working up the reaction mixture as shown in Example 1, results in the formation of methyl 18-0-ethyl-reserpate which, after recrystallization from a 1:3-mixture of benzene and cyclohexane in the presence of charcoal, melts at 221-222·5° (with decomposition).

Example 3.

The n-propyl 18-0-methyl reserpate may be prepared by reaction n-propyl reserpate with diazomethane in the presence of fluoboric acid according to the procedure described in Example 1.

The starting material may be prepared as follows: The gaseous n-diazopropane is distilled from its ether solution into a suspension of 20 g. of reserpic acid in a 1:1-mixture of chloroform and ethanol. Any excess of n-diazopropane is decomposed with acetic acid, the solvents are evaporated under reduced pressure and the residue is poured into 800 ml. of water containing 20 ml. of concentrated aqueous ammonia. A white crystalline precipitate is obtained, which is washed with water to yield the n-propyl reserpate, m.p. 164-166°.

Instead of using methyl or n-propyl reserpate other lower alkyl, *e.g.*, methyl, ethyl, n-propyl, isopropyl, n-butyl, etc. deserpidates may be used as starting materials; they may be obtained, as shown above, by esterifying deserpidic acids with lower diazoalkanes, *e.g.*, diazomethane, diazoethane, n-diazopropane, n-diazobutane and the like. Deserpidic acids to be esterified may be, for example, deserpidic acid, 9-methyl-deserpidic acid, 11-methyl-deserpidic acid, 9-methoxy-deserpidic acid, 10-methoxy-deserpidic acid, 10-methoxy-reserpic acid, 11-ethoxy-deserpidic acid, 11-n-propyloxy-deserpidic acid, 11-isopropyloxy-deserpidic acid, 11-n-butyloxy-deserpidic acid, 10,11-methylenedioxy-deserpidic acid, 10-benzyloxy-deserpidic acid, 11-benzyloxy-deserpidic acid, 11-methylmercapto-deserpidic acid, 11-ethylmercapto-deserpidic acid, 10-chloro-deserpidic acid, 5-methyl-reserpic acid, 6-methyl-deserpidic acid, 6-methyl-reserpic acid, 17-desmethoxy-17-ethoxy-reserpic acid, 17-desmethoxy-17-n-propyloxy-reserpic acid or 17-desmethoxy-17-isopropyloxy-reserpic acid, apart from reserpic acid. Upon reaction with lower diazo-alkanes, *e.g.*, diazomethane, diazoethane, n-diazopropane and the like, in the presence of fluoboric acid or another Lewis acid according to the procedure described in the previous examples these lower alkyl deserpidates furnish the corresponding lower alkyl 18-0-lower alkyl-deserpidates.

Example 4.

By reacting 2-methoxyethyl reserpate with diazomethane in the presence of fluoboric acid according to the procedure given in Example 1, the 2-methoxyethyl 18-0-methyl-reserpate may be obtained.

The starting material may be prepared as follows: To a mixture of 226 g. of a 33 per cent. aqueous solution of 2-methoxy-ethylamine and 150 ml. of diethyl ether, kept at 5° to 10° in an ice bath, is added dropwise 54 g. of ethyl chloroformate. 300 g. of a cold 40 per cent.-aqueous solution of sodium hydroxide and a second portion of 54 g. of ethyl chloroformate are given to the mixture, which is stirred for one hour. The ether layer is separated, the aqueous phase is extracted with 100 ml. of diethyl ether, and the two ether solutions are combined and dried over potassium carbonate. The solvent is evaporated under reduced pressure and the ethyl N-(2-methoxyethyl)-carbamate is distilled at 105-106°/17-20 mm.

The solution of 33 g. of ethyl N-(2-methoxyethyl)-carbamate in 200 ml. of diethyl ether are added 25 g. of cracked ice and a solution of 81 g. of sodium nitrite in 125 ml. of water. While keeping the temperature below 15°, 150 g. of 35 per cent. aqueous nitric acid is added carefully over a period of one hour. The ether layer is separated, washed with water and aqueous potassium carbonate and then dried over potassium carbonate. The residue, obtained after evaporation of the solvent under reduced pressure, represents the ethyl N-(2-methoxyethyl)-N-nitrosocarbamate, which is used without further purification.

A gently refluxing solution of 5 g. of potassium hydroxide in 15 g. of methanol and 150 ml. of diethyl ether is treated with a solution of 15·5 g. of ethyl N-(2-methoxyethyl)-N-nitroso-carbamate in 50 ml. of diethylether, which is added dropwise over a period of one hour. After refluxing for 5 minutes 100 ml. of water is added and the yellow ether solution, containing the 2-methoxy-diazoethane, is separated.

The above ether solution of 2-methoxy-diazoethane is reacted with small portions of a slurry of reserpic acid in methanol until no further reaction can be observed. A few drops of acetic acid are added, the solution is evaporated under reduced pressure and the residual oil is dissolved in ethyl acetate. Upon addition of petroleum ether a precipitate is formed, which is filtered off, dissolved in methylene chloride, which solution is washed with aqueous ammonia and filtered through a small column containing a diatomaceous earth. The residue, obtained after evaporation of the solvent is crystallized from ethyl acetate to yield the 2-methoxyethyl reserpate, m.p. 183-185°.

Instead of 2-methoxyethyl reserpate, other lower alkoxy-lower alkyl deserpidates may be used as the starting materials; they may be obtained according to the above-given procedure by using different deserpidic acids, such as, for example, deserpidic acid, 9-methyl-deserpidic acid, 11-methyl-deserpidic acid, 9-methoxy-deserpidic acid, 10-methoxy-deserpidic acid, 10-methoxy-reserpic acid, 11-ethoxy-deserpidic acid, 11-n-propyloxy-deserpidic acid, 11-n-butyloxy-deserpidic acid, 10,11-methylenedioxy-deserpidic acid, 10-benzyloxy-deserpidic acid, 11-benzyloxy-deserpidic acid, 11-methylmercapto-deserpidic acid, 11-ethylmercapto-deserpidic acid, 10-chloro-deserpidic acid, 5-methyl-reserpic acid, 6-methyl-deserpidic acid, 6-methyl-reserpic acid, 17-desmethoxy-17-ethoxy-reserpic acid, 17-desmethoxy-17-n-propyloxy-reserpic acid or 17-desmethoxy-17-isopropyloxy-reserpic acid, apart from reserpic acid. Upon reaction with lower alkoxy-lower diazoalkanes, *e.g.*, 2-methoxy-diazoethane or 2-ethoxy-diazoethane, these deserpidic acids yield the desired lower alkoxy-lower alkyl, *e.g.*, 2-methoxy-ethyl or 2-ethoxy-ethyl deserpidates, which can be converted to the lower alkoxy-lower alkyl, *e.g.*, 2-methoxy-ethyl or 2-ethoxy-ethyl, 18-0-lower alkyl-deserpidates by reaction with lower diazo-alkanes, *e.g.*, diazomethane, diazoethane, n-diazopropane and the like, in the presence of fluoboric acid or another Lewis acid according to the procedure outlined in Example 1.

Example 5.

Upon reacting methyl deserpidate with diazomethane in the presence of fluoboric acid and a mixture of ether and methylene chloride as a solvent and working up the reaction mixture according to the procedure given in Example 1, the methyl 18-0-methyl-deserpidate can be isolated.

Other lower alkyl, *e.g.*, ethyl or n-propyl and the like, deserpidates may be reacted with lower diazo-alkanes, *e.g.*, diazo-methane, diazoethane, n-diazopropane and the like, to yield other lower, *e.g.*, ethyl or n-propyl, 18-0-lower alkyl-deserpidates, *e.g.*, 18-0-ethyl-deserpidate or 18-0-n-propyl-deserpidate.

Example 6.

The 2-dimethylaminoethyl 18-0-methyl reserpate may be formed by reacting 2-dimethylaminoethyl reserpate with a

dimethyl-amino-diazoethane in the presence of fluoboric acid according to the procedure given in Example 1.

The starting material used in the above reaction may be prepared as follows: A mixture of 88 g. of a 33 per cent. aqueous N,N-dimethyl-ethylenediamine solution and 150 ml. of ether is cooled to 5° and a total of 108·5 g. of ethyl chloroformate is added in portions. A solution of 40 g. of sodium hydroxide in 60 ml. of water is given to the reaction mixture simultaneously with the second half of the ethyl chloroformate; stirring is continued for an additional hour. The ether layer is separated, the aqueous portion is extracted with ether and the ether extracts are combined and dried over anhydrous potassium carbonate. The ether is evaporated, the residue is distilled, b.p. 118-122° at 17-20 mm., to yield the ethyl N-(2-dimethylaminoethyl)-carbamate.

A solution of 40 g. of ethyl N-(2-dimethylaminoethyl)-carbamate in 125 ml. of methylene chloride is cooled to 0°, and 19·5 g. of nitrosyl chloride in 300 ml. of methylene chloride is added over a period of approximately one hour while stirring and keeping the temperature between 0° and 5°. Stirring is continued for an additional two hours, the precipitate is filtered off and recrystallized from ethyl acetate to yield ethyl N-(2-dimethylaminoethyl)-N-nitroso-carbamate hydrochloride, m.p. 133-135°.

A suspension of 11·3 g. of ethyl N-(2-dimethylaminoethyl)-N-nitroso-carbamate hydrochloride in 100 ml. of ether is added to a mixture of 40 g. of a 25 per cent. methanol solution of potassium hydroxide and 300 ml. of ether while gently refluxing. After fifteen minutes of additional heating the ether layer, containing the 2-dimethylamino-diazoethane, is decanted and immediately used.

To the above-described ether solution is added portionwise 12·0 g. of reserpic acid in methylene chloride and methanol. The mixture is allowed to stand overnight at room temperature, the solvents are evaporated under reduced pressure, and the residue is added to 400 ml. of water containing 20 ml. of ammonium hydroxide. The water solution is extracted with methylene chloride, the organic solution is filtered through a column containing a diatomaceous earth and evaporated. The 2-dimethylaminoethyl reserpate is recrystallized from a mixture of ethyl acetate and petroleum ether, m.p. 110-114°.

Instead of using 2-dimethylamino-diazoethane other tertiary amino-lower diazoalkanes, *e.g.*, 2-diethylamino-diazoethane, 3-dimethylamino-diazopropane, 2-piperidino-(N)-diazoethane or 2-morpholino-(N)-diazoethane may be used to esterify reserpic acid; other deserpidic acids, which may be esterified with the 2-dimethylamino-diazoethane or the above-mentioned diazo compounds are, for example, deserpidic acid, 9-methyl-deserpidic acid, 11-methyl-deserpidic acid, 9-methoxy-deserpidic acid, 10-methoxy-deserpidic acid, 10 methoxy-reserpic acid, 11-ethoxy-deserpidic acid, 11-n-propyloxy-deserpidic acid, 11-iso-propyloxy-deserpidic acid, 11-n-butyloxy-deserpidic acid, 10, 11-methylenedioxy-deserpidic acid, 10-benzyloxy-deserpidic acid, 11-benzyloxy deserpidic acid, 11-methylmercapto-deserpidic acid, 11-ethyl-mercapto-deserpidic acid, 10-chloro-deserpidic acid, 5-methyl-reserpic acid, 6-methyl-deserpidic acid, 6-methyl-reserpic acid, 17-desmethoxy-17-ethoxy-reserpic acid, 17-desmethoxy-17 n-propyloxy-reserpic acid or 17-desmethoxy-17-isopropyloxy-reserpic acid. The resulting tertiary amino-lower alkyl deserpidates may then be reacted with a lower diazoalkane, *e.g.*, diazomethane, diazoethane, n-diazopropane and the like, in the presence of fluoboric acid according to the procedure shown in Example 1 and the desired tertiary amino-lower alkyl 18-0-lower alkyl-deserpidates are formed.

EXAMPLE 7.

Ethyl reserpate, when reacted with diazomethane in the presence of fluoboric acid according to the procedure of Example 1, may be converted to ethyl 18-0-methyl reserpate.

Other lower alkyl 18-0-lower alkyl-reserpates, prepared according to the previously given procedure, are, for example, methyl 18-0-n-propyl-reserpate, methyl 18-0-n-butyl-reserpate, ethyl 18-0-ethyl-reserpate, ethyl 18-0-n-propyl-reserpate, ethyl 18-0-n-butyl-reserpate, n-propyl 18-0-ethyl-reserpate, n-propyl 18-0-n-propyl-reserpate, n-propyl 18-0-n-butyl-reserpate, n-butyl 18-0-methyl-reserpate, n-butyl 18-0-ethyl reserpate, n-butyl 18-0-n-propyl reserpate, n-hexyl 18-0-methyl-reserpate, n-hexyl 18-0-ethyl-reserpate and the like.

EXAMPLE 8.

The reaction of methyl reserpate with 2-methoxy-diazoethane in the presence of fluoboric acid according to the procedure of Example 1 may yield the desired methyl 18-0-(2-methoxyethyl)-reserpate.

When reacted with 2-dimethylamino-diazoethane in the presence of fluoboric acid, methyl reserpate may furnish the desired methyl 18-0-(2-dimethylaminoethyl)-reserpate.

A modification of the above procedure, comprises reacting a deserpidic acid of the formula shown in Fig. 3 of the drawings in which R_2, R_4, R_5, R_6, R_7, R'_3 and R''_3 have the above-given meaning, with a diazo-compound, such as, for example, a lower diazo-alkane, a lower alkoxy-lower diazo-alkane or a tertiary amino-lower diazo-alkane, and isolating a deserpidate compound of the formula shown in Fig. 4 of the drawings in which R_1, R_2, R_4, R_5, R_6, R_7, R'_3 and R''_3 have the above-given meaning.

This reaction may be carried out according to the previously-given procedures and is catalyzed by the necessary amount of one of the Lewis acids outlined hereinbefore. It may be advantageous to carry out the reaction in such manner that first the reactive carboxyl group in the 16-position is esterified. This may be done by adding part (one mol or an excess) of the diazo reagent to the deserpidic acid compound, using appropriate solvents, and, after the addition of the necessary Lewis acid, giving to the reaction mixture the second part (one mol or an excess) of the diazo-reagent.

The compounds of this invention may also be prepared by treating deserpidates of the formula shown in Fig. 5 of the drawings in which R_1, R_2, R_4, R_5, R_6, R_7, R'_3 and R''_3 have the previously given meaning, and R'_3 represents as reactive, esterified hydroxyl group, with an alkali metal compound of an alcohol of the formula R_8-OH, in which R_8 has the previously-given meaning.

A reactive esterified hydroxyl group is primarily a hydroxyl group esterified with a strong inorganic acid, especially a mineral acid, such as a hydrohalic acid, particularly hydrobromic or hydriodic acid. In the above-depicted starting materials R'_3 stands, therefore, advantageously for halogen, particularly for bromine or iodine.

The reactive ester group, upon treatment with an alkali metal compound of an alcohol of the formula R_8-OH, is being exchanged for an ether group, represented by the radical R_8-0-, in which R_8 has the previously-given meaning. Such alkali metal, *e.g.*, lithium, sodium or potassium, compounds of alcohols, particularly of lower alkanols, lower alkoxy-lower alkanols or tertiary amino-lower alkanols, are known and may be prepared according to known procedures, for example, by reacting the alcohol with the alkali metal. The reaction of the metal reagent with the deserpidate compound may be carried out under known conditions, preferably in the presence of an inert solvent, for example, an alcohol, *e.g.*, a lower alkanol, such as the alcohol used for the preparation of the alkali metal reagents described hereinabove. In this reaction, certain transesterification of the esterified carboxyl group in the 16-position of the deserpidate molecule may occur; in the final products R_1 and R_8 may, therefore, have identical meaning.

The starting materials used in the above reaction are known, or, if new, may be prepared according to the methods used for the manufacture of the known analogs. For example, upon treating a lower alkyl deserpidate, *e.g.*, methyl deserpidate, with a p-toluene sulfonyl halide, particularly p-toluene sulfonyl chloride, for example, in the presence of an organic base, *e.g.*, pyridine, the lower alkyl, *e.g.*, methyl, 18-0-(p-toluene sulfonyl)-deserpidate may be formed. The latter, when reacted with an alkali metal halide, *e.g.*, lithium, sodium or potassium bromide or iodide, in the presence of an inert solvent, *e.g.*, acetonitrile and the like, may be converted to the desired lower alkyl 18-desoxy-18-halogeno-deserpidate.

DEPENNING & DEPENNING,

or DEPENNING & DEPENNING.

... *Agents for the Applicants.*

Dated this 28th day of December, 1960.

MGIP Santh.—8L—69 Patent/61—6-7-62—100.

Ciba Ltd. Provisional Specification. One Sheet.

No. 74722.

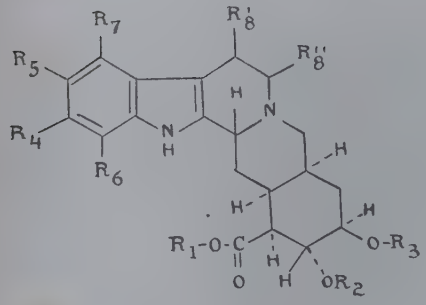

FIG. 1

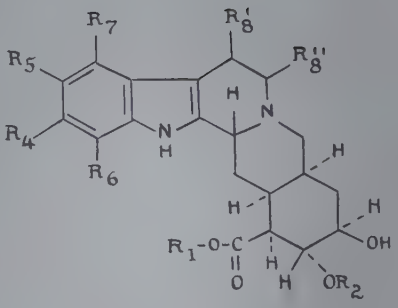

FIG. 2

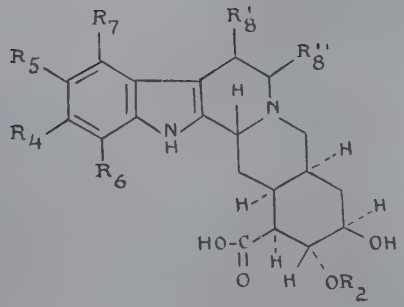

FIG. 3

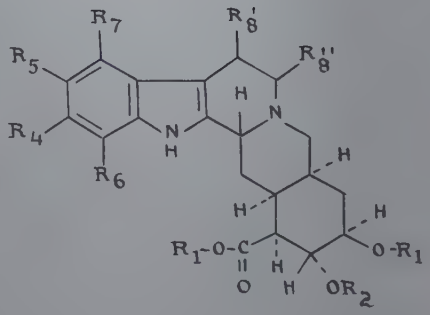

FIG. 4

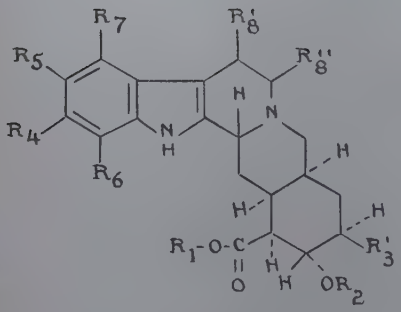

FIG. 5

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Specification No. 74723. Application No. 74723 dated 28th December 1960, (Divided out of No. 68901). [Application and Provisional Specification ante-dated to 29th August 1959. under Section 5 of the Indian Patent and Designs Act, 1911]. Complete specification left on 28th December 1960 [Complete specification ante-dated to 25th June 1960 under Section 5 of the Indian Patents and Designs Act, 1911.].

(Application accepted 28th March 1961.)

PROVISIONAL SPECIFICATION.

(Section 4)

"PHARMACEUTICAL PREPARATIONS CONTAINING NEW UREAS."

CIBA LIMITED, Chemical Manufacturers, a Swiss Corporation, of Klybeckstrasse 141, Basle, Switzerland.

The following Specification describes the nature of this invention :—

The present invention provides a process for the manufacture of new sulphonyl-ureas of the formula

$$R_1 - SO_2 - NH - CO - NH - R_2$$

in which R_1 stands for an amino group disubstituted by lower aliphatic hydrocarbon residues whose carbon chain may be interrupted by hetero atoms such as oxygen, nitrogen or sulphur, and R_2 for a lower hydrocarbon residue or oxa-hydrocarbon residue - and of their salts with bases, more especially salts with metals of groups 1 or 2 of the Periodic System, above all their alkali metal salts and alkaline earth metal salts.

Lower aliphatic hydrocarbon residues are, above all, alkyl, alkenyl, alkylene, cycloalkyl, cycloalkenyl, cycloalkylalkyl, cycloalkenyl-alkyl radicals which may contain further hydrocarbon residues, such as alkyl groups or if desired condensed benzene radicals. Residues of this kind interrupted by hetero atoms are, for example, oxa-alkyl or oxa-alkylene residues. Advantageously, these radicals contain 1 to 10 carbon atoms. As examples may be mentioned : methyl, ethyl, propyl, isopropyl, straight-chain or branched residues linked in any desired position, such as butyl, pentyl or hexyl radicals, allyl, methallyl, cyclopentyl, cyclohexyl, cyclopentenyl, cyclohexenyl, cyclohexylethyl, cyclohexenyl-ethyl, butylene-(1:4), pentylene-(1:5), hexylene-(2:5), heptylene-(2:6), 3-oxa-pentylene-(1:5), 3-oxa-butyl, 3-oxa-pentyl, 1:2-benzopentylene-(1:5), 2:3-benzopentylene-(1:5), 2-oxa-cyclopentyl-(1)-methyl and similar residues.

The lower hydrocarbon residue or oxa-hydrocarbon residue R_2 likewise contains advantageously 1 to 10 carbon atoms and is, above all, an alkyl, oxa-alkyl, alkenyl, alkinyl, cycloalkyl, cycloalkenyl, cycloalkyl-alkyl, cycloalkenyl-alkyl, phenyl-alkyl residue, and these residues may contain further hydrocarbon residues such, for example, as alkyl groups. As examples may be mentioned : methyl, ethyl, propyl, isopropyl, straight-chain or branched residues linked together in any desired position, such as butyl, pentyl or hexyl residues, allyl, methallyl, oxa-butyl or oxa-pentyl, cyclopentyl, cyclopentenyl, cyclohexyl, methylcyclohexyl, cyclohexenyl, cyclopentylmethyl, oxa-cyclo-pentylmethyl, cyclohexylmethyl residues or phenyl-ethyl residues in which the phenyl group may contain, for example halogen atoms, or lower alkyl, alkoxy or alkylmercapto groups.

The new compounds possess valuable pharmacological properties. Inter alia, they reduce the blood sugar level and are, therefore, intended to be used as antidiabetic medicaments.

Particularly valuable in this respect are the compounds of the formula shown in Fig. 1 of the accompanying drawings, and their salts, in which formula R_3 and R_4 stand for lower alkyl radicals containing 1 to 4 carbon atoms each, or R_3 and R_4 together represent a straight-chain or branched alkylene radical containing 4 to 8 carbon atoms, such as butylene-(1:4), hexylene-(2:5), pentylene-(1:5) or heptylene-(2:6), and R_5 stands for an alkyl residue containing 1 to 8 carbon atoms or a cycloalkyl radical.

A special object of the present invention are the compounds, having an especially good blood sugar lowering action, of the formula

$$R_6 - SO_2 - NH - CO - NH - R_7$$

and their salts, in which formula R_6 stands for a pyrrolidino or piperidino residue and R_7 for a cyclopentyl or cyclohexyl residue, above all the N-(piperidino-sulphonyl)-N'-cyclohexyl urea of the formula shown in Fig. 2 of the drawings, and its salts.

The new compounds are made by processes as such known. Preferably, a compound each of the formlae

$$R_1 - SO_2X \text{ and } Y - R_2$$

are reacted together, in which formulae X and Y are residues that react together with formation of the group -NH-CO-NH- which connects the aforementioned residues R_1-SO_2- and R_2. Advantageously either the residuo X or the residue Y is a free amino group and the other is a reactive derivative of the carboxy-amino residue of the formula

$$-N - COOH.$$
$$\boxed{\ }$$

Such derivatives are, for example, esters, such as alkyl or phenyl esters, halides, such as chlorides or bromides, the inner anhydride of the formula $-N=C=O$, amides, more especially acylamides such as alkanoylamides, aroylamides or sulphonylamides.

According to another process, in a compound of the formula

$$R_1 - SO_2 - NH - \underset{\displaystyle X}{\overset{\displaystyle \|}{C}} - NH - R_2$$

or

$$R_1 - SO_2 - N = \underset{\displaystyle X'}{\overset{\displaystyle |}{C}} - NH - R_2$$

or in a tautomer of such a compound, in which R_1 and R_2 have the above meaning and X or X' represents a substituent convertable into an oxo group accompanied by dissolution of the C=N double bond, said substituent is converted into an oxo group. Inter alia, an appropriate guanidine can be hydrolysed or a thiourea converted into an urea by treatment with ammonia, if desired after or by simultaneous treatment with a desulphurising agent, such as a heavy-metal oxide or a salt thereof, such as a lead, copper, silver or mercury compound, or etherified isourea can be hydrolysed.

The aforementioned processes are carried out in the conventional manner, in the presence or absence of a diluent and/or condensing agent, at a low, ordinary or elevated temperature, if desired under superatmospheric pressure. In these processes one starting material may be formed in the course of the reaction.

According to a preferred variant of the process a sulphonamide of the formula $R_1 - SO_2 - NH_2$, advantageously in the form of a metal salt, such as an alkali metal salt, thereof is reacted with an isocyanate of the formula OCN-R_2 which latter, if desired, can be formed, for example, in the course of the reaction.

Alternatively, an isocyanate of the formula R_1-NCO or a urethane of the formula R_1-NH-COOR' (in which R' represents an ester residue, for example an alkyl or aryl radical), or a carbamic acid halide of the formula

$$R_1 - SO_2 - NH - CO - Hal$$

or a urea of the formula

$$R_1 - SO_2 - NH - \underset{\displaystyle O}{\overset{\displaystyle \|}{C}} - NH - Ac$$

(in which Ac stands for an acyl radical, for example one of those mentioned above) may be reacted with the amine of the formula $H_2N\text{-}R_2$. It is also possible to react, for example, a sulphonamide of the formula $R_1 - SO_2 - NH_2$ with a urethane of the formula $R_2 - NH - COOR'$ (in which R' has the above meaning) or with a halide of the formula $R_2 - NH - CO - Hal$ or with a urea of the formula $R_2 - NHCONH_2$.

The starting materials are known or can be made by as such known method. Preferred starting materials are those which yield the final products designated above as particularly valuable.

The invention includes also any modification of the process in which an intermediate obtained at any stage of the process is used as starting material and the remaining step or steps is or are carried out, or the process is terminated at any stage thereof, or in which the starting materials are formed in the course of the reaction.

Depending on the reaction conditions employed, the new compounds are obtained in the free form or as salts. Salts thus obtained can be converted into the free compounds in the usual manner, for example by acidification. The salts can be converted into salts thereof, such as salts with bases, for example ammonia or organic bases, and more especially into the aforementioned metal salts, for example those of sodium, potassium, calcium or magnesium.

The new compounds and salts thereof can be used in the form of pharmaceutical preparations.

The following Examples illustrate the invention.

Example 1.

A mixture of 6 grams of piperidino sulphonamide, 5 grams of potassium carbonate and 75 cc of acetone is boiled for 1 hour. 6 grams of butyl isocyante are then added, and the whole is heated for 4 hours at 60°. The reaction mixture is then evaporated, the residue is treated with 2N-sodium hydroxide solution, and the undissolved matter is filtered off. Acidification of the filtrate causes the N-(piperidino-sulphonyl)-N'-n-butylurea of the formula shown in Fig. 3 of the drawings, to separate out in crystalline form. Upon recrystallisation from methylene chloride + petroleum ether it melts at 111-112°C.

Example 2.

A solution of 10 grams of piperidino sulphonamide in 100 cc of acetone is stirred with 9 grams of potassium carbonate for 1 hour at the boil. 9 grams of ethyl isocyanate are then added, and the mixture is heated for 2 hours at 50°. The reaction mixture is evaporated to dryness in vacuo, and the residue is treated with 100 cc of 2N-sodium hydroxide solution. The precipitate is filtered off, and the filtrate is treated with 2N-hydrochloric acid to reach a pH of 1 to 2. The crystalline precipitate thus formed is the N-(piperidino-sulphonyl)-N'-ethyl-urea of the formula shown in Fig. 4 of the drawings, which, after recrystallisation from water, melts at 134-136°C.

Example 3.

A solution of 6 grams of piperidino sulphonamide in 75 cc of acetone is stirred for 1 hour at the boil with 5 grams of finely powdered potassium carbonate. 10 grams of cyclohexyl isocyanate are then added, and the whole is heated for 4 hours at 60°. The reaction mixture is evaporated to dryness, the residue is treated with 100 cc of 2N-sodium hydroxide solution, and the precipitate formed is filtered off. On acidifying the filtrate with 2N-hydrochloric acid, N-(piperidino-sulphonyl)-N'-cyclohexyl-urea of the formula shown in Fig. 2 of the drawings, is obtained in crystalline form. After having been recrystallised from petroleum ether it melts at 141-143°C.

Example 4.

A solution of 8 grams of piperidino sulphonamide in 75 cc of acetone is stirred for 1 hour at the boil with 5 grams of finely powdered potassium carbonate. 10 grams of β-phenylethyl isocyanate are then added, and the mixture is heated for 4 hours at 60°C. The reaction mixture is evaporated to dryness, the residue is treated with 100 cc of 2N-sodium hydroxide solution, and the precipitate formed is filtered off. When the filtrate is acidified with 2N-hydchloric acid, the N-(piperidino-sulphonyl)-N'-(β-phenylethyl)-urea of the formula shown in Fig. 5 of the drawings separates out as a viscid oil which crystallises after standing for some time. After recrystallisation from ethanol, it melts at 136-138°C.

Example 5.

A solution of 8 grams of piperidine sulphonamide in 75 cc of acetone is boiled for 1 hour with 5 grams of potassim carbonate. 10 grams of 2:4-dimethyl-pentyl-(3)-isocyanate are added and the whole is heated for 4 hours at 60°C. The reaction mixture is then evaporated to dryness, the residue is treated with 100 cc of 2N-sodium hydroxide solution, and the precipitate formed is filtered off. When the filtrate is acidified with 2N-hydrochloric acid, the N-(piperidino-sulphonyl)-N'-[2:4-dimethyl-pentyl-(3)]-urea of the formula shown in Fig. 6 of the drawings, separates out in crystalline form. After recrystallisation from alcohol it melts at 156-157°C.

B. Depenning
of DePENNING & DePENNING,
Agents for the Applicants.

Dated this 28th day of December 1960.

COMPLETE SPECIFICATION.

(Section 4)

Specification No. 74723.

" PHARMACEUTICAL PREPARATIONS CONTAINING NEW UREAS. "

CIBA LIMITED, Chemical Manufacturers, a Swiss Corporation, of Klybeckstrasse, 141, Basle, Switzerland.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

The present invention provides new pharmaceutical preparations containing new sulfonyl-ureas of the formula

$$R_1\text{—}SO_2\text{—}NH\text{—}CO\text{—}NH\text{—}R_2$$

—in which R_1 stands for an amino group disubstituted by lower aliphatic hydrocarbon radicals containing 1-10 carbon atoms, whose carbon chain may be interrupted by hetero atoms such as oxygen, nitrogen or sulfur, and R_2 for a lower hydro-carbon radical or oxa-hydrocarbon radical containing 1-10 carbon atoms, or their salts with bases, more especially salts with metals of groups 1 or 2 of the Periodic System, above all their alkali metal salts and alkaline earth metal salts, or mixtures thereof, the manufacture of these compounds is disclosed and claimed in our specification No. 68901 of which the present application is a divisional.

The new pharmaceutical preparations of the invention possess valuable pharmacological properties. They reduce the

blood sugar level and are, therefore, intended to be used as antidiabetic medicaments.

Especially valuable are those preparations which contain sulfonylureas of the above formula, wherein the hydrocarbon radicals of the groups R_1 and R_2 are as follows:

Lower aliphatic hydrocarbon radicals are, above all, such as contain 1-10 carbon atoms, e.g., alkyl, alkenyl, alkylene, cycloalkyl, cycloalkenyl, cycloalkyl-alkyl, cycloalkenyl-alkyl radicals which may contain further hydrocarbon radicals, such as alkyl groups or if desired fused on benzene radicals. Radicals of this kind interrupted by hetero atoms are, for example, oxa-alkyl or oxa-alkylene radicals. As examples, may be mentioned: methyl, ethyl, propyl, isopropyl, straight-chain or branched radicals linked in any desired position, such as butyl, pentyl, hexyl or heptyl radicals, allyl, methallyl, cyclopentyl, cyclohexyl, cyclopentenyl, cyclohexenyl, cyclopentyl-methyl, oxa-cyclopentyl-methyl, such as 2-oxa-cyclopentyl-(1)-methyl, cyclohexylmethyl, methyl-cyclohexyl, cyclohexylethyl, cyclohexenyl-ethyl, butylene-(1:4), pentylene-(1:5), hexylene-(1:6), hexylene-(2:5), heptylene-(2:6), 3-oxa-pentylene-(1:5), 3-oxa-butyl, 3-oxa-pentyl, 1:2-benzopentylene-(1:5), 2:3-benzopentylene-(1:5), and similar radicals.

The lower hydrocarbon radical or oxa-hydrocarbon radical R_2 likewise contains advantageously 1 to 10 carbon atoms and is, above all, an alkyl, oxa-alkyl, alkenyl, alkinyl, cycloalkyl, cycloalkenyl, cycloalkyl-alkyl, cycloalkenyl-alkyl, phenyl-alkyl radical, and these radicals may contain further hydrocarbon radicals such, for example, as alkyl groups. As examples may be mentioned: methyl, ethyl, propyl, isopropyl, straight-chain or branched radicals linked together in any desired position, such as butyl, pentyl, hexyl or heptyl radicals, allyl, methallyl, cyclopentyl, cyclohexyl, cyclopentenyl, cyclohexenyl, cyclopentyl-methyl, oxa-cyciopentyl-methyl, such as cyclohexylmethyl, methyl-cyclohexyl, cyclohexylmethyl, cyclohexenyl-ethyl, 3-oxa-butyl, 3-oxa-pentyl or phenyl-ethyl radicals in which the phenyl group may contain, for example halogen atoms, such as fluorine, chlorine, bromine, trifluoromethyl, or lower alkyl, alkoxy or alkylmercapto groups in which the alkyl groups contain, for example 1 to 3 carbon atoms.

The invention envisages in the first place those preparations which contain as active components the compounds of the formula shown in Fig. 1 of the drawings accompanying the provisional specification, or salts or mixtures thereof, in which formula R_3 and R_4 stands for lower alkyl radicals containing 1 to 4 carbon atoms each, or R_3 and R_4 together represent a straight-chain or branched alkylene or oxa-alkylene radical containing 4 to 8 carbon atoms, such as butylene-(1:4), pentylene-(1:5), hexylene-(1:6), hexylene-(2:5), heptylene-(2:6) or 3-oxa-pentylene-(1:5) and R_5 stands for an alkyl radical containing 1 to 8 carbon atoms, a phenylethyl radical or a cycloalkyl radical and even more preferred of the formula

$$R_6\text{-}SO_2\text{-}NH\text{-}CO\text{-}NH\text{-}R_7$$

and their salts, in which formula R_6 stands for a pyrrolidino, piperidino or morpholino radical and R_7 for a cyclopentyl, cyclohexyl or phenylethyl radical, above all the N-(piperidino-sulfonyl)-N'-cyclohexyl urea of the formula thown in Fig. 2 of the drawings accompanying the provisional specification, or salts or mixtures thereof.

The most valuable preparations however are those which contain as active ingredient the N-(morpholino-sulfonyi)-N'-(β-phenyl-ethyl)-urea, or salts or mixtures thereof.

The new preparations contain the active ingredient in admixture with a pharmaceutical organic or inorganic carrier suitable e.g. for enteral administration. As carriers such substances may be employed as do not react with the new compounds, such as water, gelatine, lactose, starches, magnesium stearate, talc, vegetable oils, benzyl alcohols, gums, polyalkylene glycols, white petroleum jelly, cholesterol or any other known carrier for medicaments. The pharmaceutical preparations may be in the form, for example, of tablets, dragees, powder or suppositories or in liquid form as solutions, suspensions or emulsions. The preferred forms of the new preparations are those of tablets, capsules or sirups. The new preparations contain 50-2000 mg of the active ingredient per dosage unit. Usually, a daily dose of 0.1—2 g of the active ingredient is appropriate. Preparations containing the N-(morpholino-sulfonyl)-N'-(β-phenyl-ethyl)-urea are preferably employed in a dosage of 0.5-1 g of the active ingredient per day. These of course are average doses. The practicing physician may depart therefrom according to the particular situation. The new preparations contain the active ingredients in an amount of 30-95% per weight, if preparations with solid carriers are envisaged, and in an amount of 5-50%, if liquid carriers are involved. Preferred preparations with solid carriers, e.g. tablets or capsules contain 60-95% of the active ingredient, preferred preparations with liquid carriers, e.g. sirups, contain from 5 to 20% of the active ingredient.

The preparations are made in the usual manner. The manufacture of the active ingredients is carried out according to the process of Specification No. 68901 e.g. a sulfonamide of the formula $R_1\text{-}SO_2\text{-}NH_2$, advantageously in the form of a metal salt, such as an alkali metal salt, thereof is reacted with an isocyanate of the formula $OCN\text{-}R_2$ which latter, if desired, can be formed, for example, in the course of the reaction, R and R_1 having the meanings given above.

The following Example illustrates the invention.

Example

The following homogenous mixture can be filled in portions of 270 mg into capsules:

N-(morphalino-sulfonyl)-N'-(β-phenyl-ethyl)-urea	250.0 g
Talcum	12.5 g
Stearic acid	7.5 g
	270.0 g

These capsules can be administered in a dose of 0.5—1 g of the active ingredient per day for the treatment of diabetes.

The active ingredient is prepared as follows:

A solution of 9 g of morpholino sulfamide in 75 cc of acetone is boiled and stirred for 1 hour with 5 g of finely powdered potassium carbonate. 10 g of β-phenylethyl isocyanate in 25 cc of acetone are then added, and the whole heated at 60°C for 4 hours. The reaction mixture is evaporated to dryness, the residue mixed with 100 cc of 2N-sodium hydroxide solution and filtered. On acidification of the filtrate, the N-(morpholino-sulfonyl)-N'-(β-phenylethyl)-urea of the formula shown in the drawing accompanying this specification, separates out in the form of crystals. After recrystallization from ethanol the compound melts at 142°C.

In the same manner preparations containing the following ureas as active ingredients can be made:

N-(piperidino-sulfonyl)-N'-n-butylurea,
N-(piperidino-sulfonyl)-N'-ethyl-urea,
N-(piperidino-sulfonyl)-N'-cyclohexyl-urea,
N-(N-(piperidino-sulfonyl)-N'-(β-phenylethyl)-urea,
N-(piperidino-sulfonyl)-N'-[2:4-dimethyl-pentyl-(3)]-urea,
N-(morpholino-sulfonyl)-N'-n-butyl-urea,
N-(pyrrolidino-sulfonyl)-N'-ethyl-urea,
N-(pyrrolidino-sulfonyl)-N'-cyclohexyl-urea,
N-(di-n-propylamino-sulfonyl)-N'-(β-phenylethyl)-urea,
N-(di-n-propylamino-sulfonyl)-N'-cyclohexyl-urea,
N-(hexamethylene-imino-sulfonyl)-N'-cyclohexyl-urea,
N-(1,2,3,4-tetrahydro-isoquinolino-sulfonyl)-N'-n-butyl-urea.

The preparation of these active ingredients is disclosed in the above referred-to specification.

WE CLAIM:—

1. Pharmaceutical preparations for the treatment of diabetes, containing new sulfonyl-ureas of the formula

$$R_1\text{-}SO_2\text{-}NH\text{-}CO\text{-}NH\text{-}R_2$$

-in which R_1 stands for an amino group disubstituted by lower aliphatic hydrocarbon radicals containing 1-10 carbon atoms, whose carbon chain may be interrupted by hetero atoms such as oxygen, nitrogen or sulfur, and R_2 for a lower hydrocarbon

radical or oxa-hydrocarbon radical containing 1-10 carbon atoms, or their salts with bases, more especially salts with metals of groups 1 or 2 of the Periodic System, above all their alkali metal salts and alkaline earth metal salts or mixtures thereof in admixture with a pharmaceutical solid carrier.

2. Pharmaceutical preparations for the treatment of diabetes, containing new sulfonyl-ureas of the formula

$$R_1\text{-}SO_2\text{-}NH\text{-}CO\text{-}NH\text{-}R_2$$

-in which R_1 stands for an amino group disubstituted by lower aliphatic hydrocarbon radicals containing 1-10 carbon atoms, whose carbon chain may be interrupted by hetero atoms such as oxygen, nitrogen or sulfur, and R_2 for a lower hydrocarbon radical or oxa-hydrocarbon radical containing 1-10 carbon atoms or their salts with bases, more especially salts with metals of groups 1 or 2 of the Periodic System, above all their alkali metal salts and alkaline earth metal salts or mixtures thereof in admixture with a liquid pharmaceutical carrier, said preparations containing from 5 to about 50% of the active ingredient.

3. Pharmaceutical preparations for the treatment of diabetes, containing new sulfonyl-ureas of the formula

$$R_1\text{-}SO_2\text{-}NH\text{-}CO\text{-}NH\text{-}R_2$$

- in which R_1 stands for an amino group disubstituted by lower aliphatic hydrocarbon radicals containing 1-10 carbon atoms, whose carbon chain may be interrupted by hetero atoms such as oxygen, nitrogen or sulfur, and R_2 for a lower hydrocarbon radical or oxa-hydrocarbon radical containing 1-10 carbon atoms or their salts with bases, more especially salts with metals of groups 1 or 2 of the Periodic System, above all their alkali metal salts and alkaline earth metal salts or mixtures thereof in admixture with a liquid pharmaceutical carrier, said preparations containing from about 5 to about 20% of the active ingredient.

4. Tablets for the treatment of diabetes. containing new sulfonyl-ureas of the formula

$$R_1\text{-}SO_2\text{-}NH\text{-}CO\text{-}NH\text{-}R_2$$

- in which R_1 stands for an amino group disubstituted by lower aliphatic hydrocarbon radicals containing 1-10 carbon atoms, whose carbon chain may be interrupted by hetero atoms such as oxygen, nitrogen or sulfur, and R_2 for a lower hydro-carbon radical or oxa-hydrocarbon radical containing 1—10 carbon atoms or their salts with bases, more especially salts with metals of groups 1 or 2 of the Periodic System, above all their alkali metal salts and alkaline earth metal salts or mixtures thereof in admixture with a solid pharmaceutical carrier.

5. Capsules for the treatment of diabetes, containing new sulfonyl-ureas of the formula

$$R_1\text{-}SO_2\text{-}NH\text{-}CO\text{-}NH\text{-}R_2$$

- in which R_1 stands for an amino group disubstituted by lower aliphatic hydrocarbon radicals containing 1-10 carbon atoms, whose carbon chain may be interrupted by hetero atoms such as oxygen, nitrogen or sulfur, and R_2 for a lower hydrocarbon radical or oxa-hydrocarbon radical containing 1-10 carbon atoms or their salts with bases, more especially salts with metals of groups 1 or 2 of the Periodic System, above all their alkali metal salts and alkaline earth metal salts or mixtures thereof in admixture with a solid pharmaceutical carrier.

6. Syrups for the treatment of diabetes, containing new sulfonyl-ureas of the formula

$$R_1\text{-}SO_2\text{-}NH\text{-}CO\text{-}NH\text{-}R_2$$

- in which R_1 stands for an amino group disubstituted by lower aliphatic hydrocarbon radicals containing 1-10 carbon atoms, whose carbon chain may be interrupted by hetero atoms such as oxygen, nitrogen or sulfur, and R_2 for a lower hydrocarbon radical or oxa-hydrocarbon radical containing 1-10 corbon atoms or their salts with metals of groups 1 or 2 of the Periodic System, above all their alkali metal salts and alkaline earth metal salts or mixtures thereof in admixture with a liquid pharmaceutical carrier, said compositions containing from 5 to about 50% of the active ingredient.

7. Pharmaceutical preparations as claimed in claim 1 which contain 30-95% of the active ingredient.

8. Pharmaceutical preparations as claimed in claim 1 which contain 60-95% of the active ingredient.

9. Pharmaceutical preparations as claimed in claims 2 and 3, which contain 5-20% of the active ingredient.

10. Tablets for the treatment of diabetes as claimed in claim 4 containing 30-95% of the active ingredient.

11. Tablets for the treatment of diabetes as claimed in claim 4 containing 60-95% of the active ingredient.

12. Capsules for the treatment of diabetes as claimed in claim 5 containing 30-95% of the active ingredient.

13. Capsules for the treatment of diabetes as claimed in claim 5 containing 60-95% of the active ingredient.

14. Syrups for the treatment of diabetes as claimed in claim 6 containing 5-50% of the active ingredient.

15. Syrups for the treatment of diabetes as claimed in claim 6 containing 5-20% of the active ingredient.

16. A pharmaceutical preparation as claimed in claims 1-15, wherein the active ingredient is one or more of the compounds of the formula shown in Fg. 1 of the drawings accompanying the provisional specification, in which formula R_3 and R_4 stands for lower alkyl radicals containing 1 to 4 carbon atoms each, or R_3 and R_4 together represent a straight-chain or branched alkylene or oxa-alkylene radical containing 4 to 8 carbon atoms, such as butylene-(1:4), pentylene-(1:5), hexylene-(1:6), hexylene-(2:5). heptylene-(2:6) or 3-oxa-pentylene-(1:5), and R_5 stands for an alkyl radical containing 1 to 8 carbon atoms, a phenylethyl radical or a cycloalkyl radical.

17. A pharmaceutical preparation as claimed in claims 1-15, wherein the active ingredient is one or more of

$$R_6\text{-}SO_2\text{-}NH\text{-}CO\text{-}NH\text{-}R_7$$

and their salts, in which formula R_6 stands for a pyrrolidino, piperidino or morpholino radical and R_7 for a cyclopentyl, cyclohexyl or phenylethyl radical.

18. A pharmaceutical preparation as claimed in claims 1-15, wherein the active ingredient is N-(piperidino-sulfonyl)-N'-cyclohexyl urea.

19. A pharmaceutical preparation as claimed in claims 1-15, wherein the active ingredient is N-(morpholinosulfonyl)-N'-(β-phenyl-ethyl)-urea.

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Agents for the Applicants.

Dated this 28th day of December 1960.

Printed by The Nelya Printing Works, Calcutta-1.

Ciba Ltd.
No. 74723.

Provisional Specification.

One Sheet.

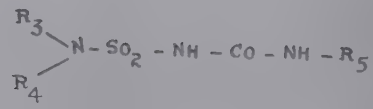

FIG. 1

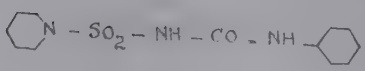

FIG. 2

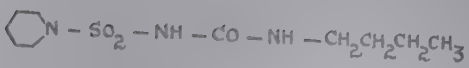

FIG. 3

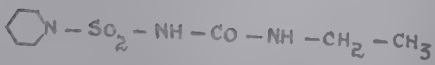

FIG. 4

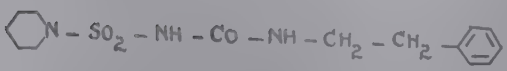

FIG. 5

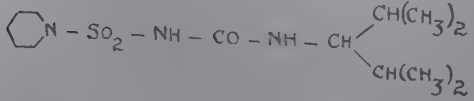

FIG. 6

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Ciba Ltd. Complete Specification. One Sheet.

No.74723.

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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74724. Application No. 74724 dated 29th December 1960.
Complete Specification left on 12th January 1961. (Application accepted 19th September 1962.)

PROVISIONAL SPECIFICATION.

A NOVEL DEVICE FOR LIFTING LARGE QUANTITIES OF FILTERED WATER FROM UNDERGROUND WATER BEARING STRATA.

AUTHUOUDY CHINNATHAMBU JAYARAJ, Municipal Engineer, Tillainagar, Tiruchirapalli, Madras Province.
A subject of the Indian Republic.

The following specification describes the nature of this invention

The invention relates to collection of large quantities of filtered water from the underground water bearing strata for drinking and other use of the public as well as for industrial and irrigation needs.

Basing on the principle of the syphon, water from the deep water bearing strata is lifted up and discharged into suitably located cisterns, tanks or tubs As the water in these receptacles is pumped out more water flows in through a system of syphons continuous and coming up from deep tube wells. The discharge from the system increases with the water level in the tub getting lower and lower.

Figure 1 of the accompanying drawings represents a plan of the invention and shows the wells, tub and the syphon pipes. Figure 2 is an elevation showing the comparative depth of wells, tub and the syphon pipes along with their relative positions. A well (1) (see Figure 2 for numbers) is sunk in the water bearing strata (2) to as much depth as is possible for enabling a tub to be put to that depth. This tub (3) which will tend to fleet should be lowered and anchored In and around the well a series of deep tube wells (4) with slotted pipes (5) attached at bottom are put and the tubes of these tube wells are continued up without break and then turned towards the tub and ultimately syphoned into it. (The numbers in Figure 1 refer to the same description as the numbers of Figure 2). This way more and more tube wells can be erected and these can be continued up and syphoned into the tub thereby increasing the discharge into the tub. So long as the aquifer is rich and fertile as in a flowing river with deep sandy or previous strata large quantity of filtered water can be collected by this process.

Besides freedom from contamination the area needed for working this process is comparatively very small than those of the orthodox systems of infiltration wells or galleries.

While the slotted pipe should be as big as is convenient to put number of slots, the rigid pipe that comes up and forms the syphons may be reduced in size to suit the expected discharge.

While the Figure 1 attached shows a number of syphons, the Figure 2 shows only two to avoid confusion.

Sd. ILLEGIBLE.

Dated this 21st day of December 1960

COMPLETE SPECIFICATION.

A NOVEL DEVICE FOR LIFTING LARGE QUANTITIES OF FILTERED WATER FROM UNDERGROUND WATER BEARING STRATA.

AUTHUOUDY CHINNATHAMBU JAYARAJ, Municipal Engineer, Tillainagar, Tiruchirapalli, Madras Province.
A subject of the Indian Republic.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

The invention relates to collection of large quantities of filtered water from the underground water bearing strata for drinking and other use of the public as well as for industrial and irrigation needs.

Basing on the principle of the syphon, water from the deep water bearing strata is lifted up and discharged into suitably located cisterns, tanks or tubs. As the water in these receptacles is pumped out more water flows in through a system of syphons continuous and coming up from deep tube wells The discharge from the system increases with the water level in the tub getting lower and lower.

Figure 1 of the accompanying drawings represents a plan of the invention and shows the wells, tub and the syphon pipes. Figure 2 is an elevation showing the comparative depths, of wells, tub and the syphon pipes along with their relative positions

A well (1) (Figure 2) is sunk in the water bearing strata (2) to as much depth as is possible for enabling a tub to be put to that depth. This tub (3) which will tend to float should be lowered and anchored In and around the well a series of deep tube wells (4) at close intervals say 2 or 3 feet apart wich slotted pipes (5) attached at bottom are put and the tubes of these tube wells are continued up without break and then turned towards the tub and ultimately syphoned into it. (The numerals of Figure 1 refer to the same parts as they refer to in Figure 2). This may more and more tube wells can be erected and all these can be individually continued up and syphoned into the tub thereby increasing the discharge into the tub. So long as the aquifer is rich and fertile as in a flowing river with deep sandy or pervious strata large quantity of filtered water can be collected by this process. The bigger outer well shown in Figure 1 is only to retain side earth to facilitate tube well sinking operations. The invention is simple having a deep tub at centre with series of deep bore wells discharging water into it. Besides freedom from contamination, the area needed for working this process is comparatively very small than these of the orthodox systems of infiltration wells or galleries

While the slotted pipe should be as big as is convenient to put numerous slots the pipe that comes up and forms the syphon may be reduced in size to suit the expected discharge.

While the Figure 1 attached shows a number of syphons the Figure 2 shows only two to avoid confusion.

I claim:

A device for lifting large quantities of filtered water by a system of continuous and well joined pipes bringing up the underground waters and syphoning into a central tub thereby getting any quantity of filtered and uncontaminated water from underground source wherein a deep central tub having all around it a multiple number of deep bore wells and all these are individually brought up and made to syphon into the tub and thereby each such well contributing a certain quantity swell up total discharge.

Sd. ILLEGIBLE.

Dated this 9th day of January 1961.

Price: TWO RUPEES.

MGIPC—L—154 Patent/62—22-8-62—100.

COMPLETE

NUMBER OF SHEETS 2.
SHEET Nº 1

NAME OF APPLICANT:- AUTHUCUDY CHINNATHAMBU JAYARAJ

Nº 74724.

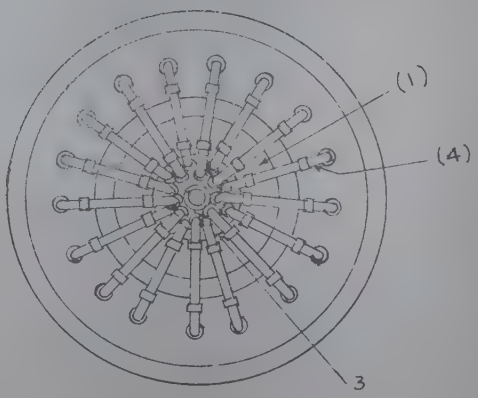


FIG 1.

A.C JAYARAJ

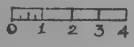
REG. NO. 2273 E 41 100-64

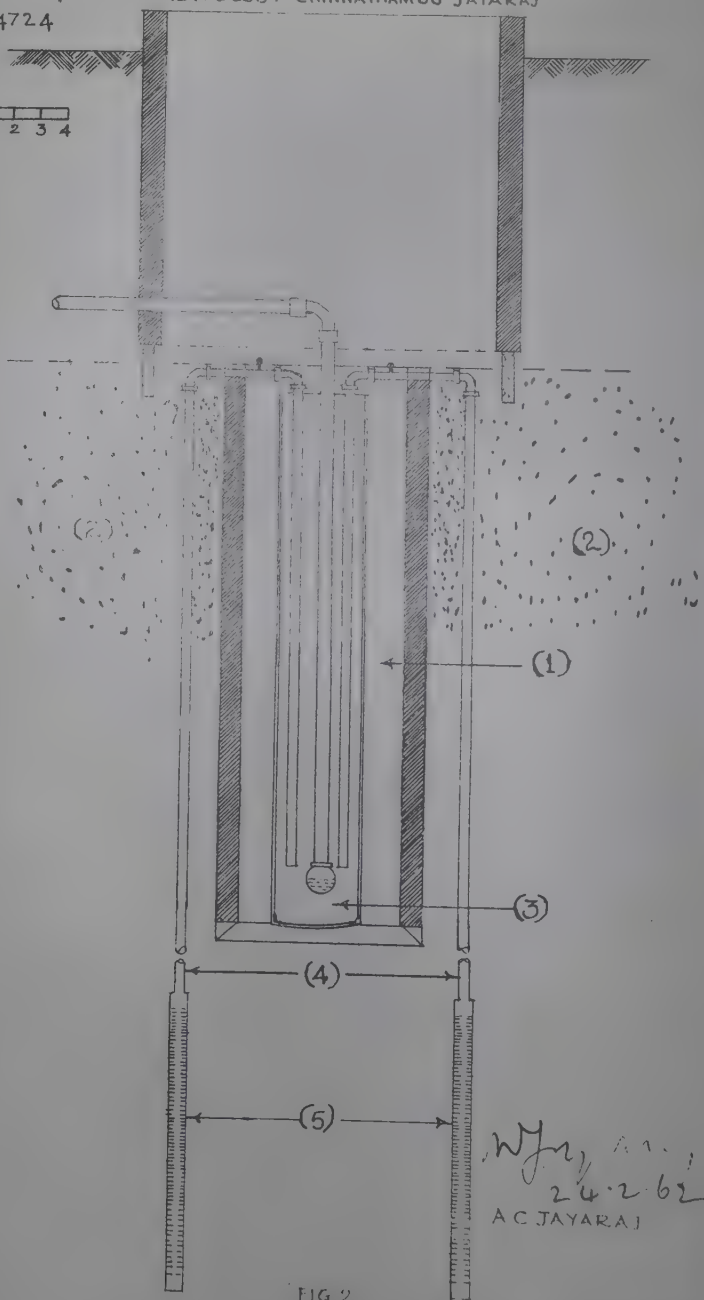
COMPLETE.

NUMBER OF SHEETS 2.
SHEET NO ..... 2.

NAME OF APPLICANT:- AUTHUCUDY CHINNATHAMBU JAYARAJ

No. 74724





24.2.62
A C JAYARAJ

FIG 2.

REG. NO. 2273 E/44—106'64

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PROVISIONAL NUMBER OF SHEETS 2.
SHEET NO. 1.

NAME OF APPLICANT:- AUTHUCUDY CHINNATHAMBU JAYARAJ

No. 74724.

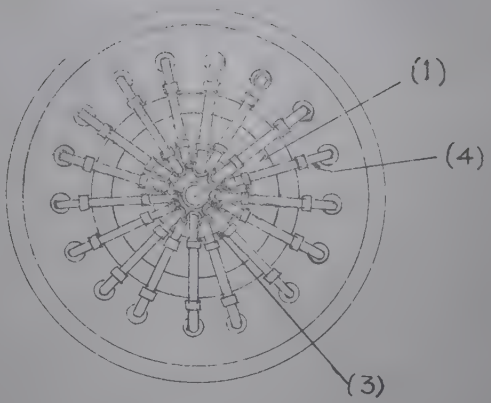

FIG.1

24-2-62
A.C.JAYARAJ.

REG. NO. 2273 E 44 -1(1) 64

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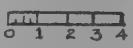
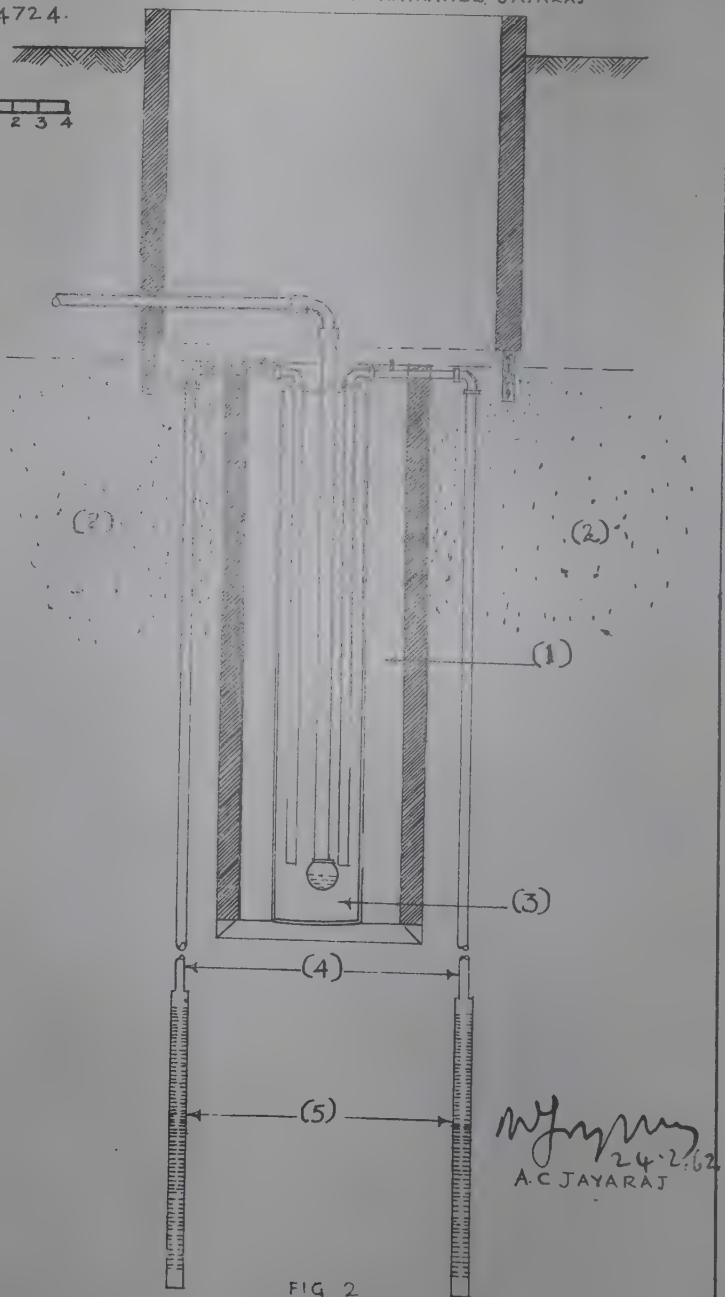
PROVISIONAL

NUMBER OF SHEETS 2.
SHEET No. 2

NAME OF APPLICANT:- AUTHUCUDY CHINNATHAMBU JAYARAJ

No 74724.





24.2.62
A.C JAYARAJ

FIG 2

REG. NO. 2273 E·44—106·64.

PRINTED AT THE SURVEY OF INDIA OFFICES. (P L O)

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.
Specification No. 74725. Application No. 74725, dated 29th December 1960. Complete Specification left on 20th October 1961. (Application accepted 14th December 1961.)

PROVISIONAL SPECIFICATION

(Section 4)

"AN IMPROVED VACUUM FLASK OR LIKE CONTAINER."

ALIMAHOMED CHHAGANBHAI PADAMSEE, Indian National, C/o. Messrs. Salemahomed Padamsee and Company, 141, Sheriff Devji (Chuckla) Street, City of Bombay, State of Maharashtra, India.

The following Specification describes the nature of this invention:—

This invention relates to an improved vacuum flask or like container which comprises of a bottle of glass provided within an outer casing or canister and which are especially used for containing and storing beverages or the like.

When such vacuum flasks or like containers are to be used at night in a sick room, besides a sick bed, it is found inconvenient to either empty or fill the vacuum flask in the dark, as by putting on a light for the said purpose is likely to disturb the patient.

This invention provides for a vacuum flask fitted with a contrivance which is provided with a light and also with an arrangement which automatically switches on the said light when the said flask is lifted from its resting place, and which continues to burn until the said flask is replaced on the table or any such resting place.

The canister of the vacuum flask according to this invention is provided with a false bottom into which the said contrivence is fitted. The said contrivance consists of storage batteries connected to an electric bulb, through a spring loaded switch. The knob of the spring loaded switch protudes out through the bottom of the said contrivance, outside the base of the canister, when the said contrivance is fitted into the false bottom of the canister. That portion of the canister which comes against the electric bulb of the said contrivance, is provided with a window.

The knob of the spring loaded switch when it protrudes outside the base of the canister, in its extended position, such as, when the flask is lifted from its resting place, completes the electrical circuit and the bulb of contrivance glows, instantaneously. When the flask is replaced on any flat surface, the knob of the spring loaded switch is automatically pushed in, and thereby the circuit broken and the said bulb goes off.

The said contrivance can also be, in emergencies, put to use as a torch lamp. This is done by detaching the said contrivance from the canister bottom, when it can be conveniently carried about from place to place and used as a pocket-torch.

ALIMAHOMED CHHAGANBHAI PADAMSEE,
By P. S. PAI & CO.
Authorised Agents.

Dated this 26th day of December 1960.

COMPLETE SPECIFICATION

(Section 4)

Specification No. 74725.

"AN IMPROVED VACUUM FLASK OR LIKE CONTAINER."

ALIMAHOMED CHHAGANBHAI PADAMSEE, Indian National, C/o. Messrs. Salemahomed Padamsee and Company, 141 Sheriff Devji (Chuckla) Street, City of Bombay, State of Maharashtra, India.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This invention relates to vacuum flasks or like containers which comprise vacuum bottles of glass housed in outer casings or canisters. Such vacuum flasks are used for storing hot or cold liquids for example, beverages and are especially useful for keeping beverages for the sick. However, for pouring off the liquid from a vacuum flask kept by the side of a sick bed, a light in the sick room will have to be put on which would disturb the patient; similar difficulty will be experienced if the flask is to be filled afresh with the beverage for the patient.

The object of my invention is to provide a vacuum flask with an electric light or illuminating device which is automatically switched on when the flask is lifted off its resting place for example, a table or a stand, and which automatically switched off when the flask is replaced on its resting place.

A vacuum flask, according to my invention comprises an outer casing or canister having a false bottom in which is housed an electric lighting or illuminating device which consists of an electric incandescent bulb, one or more primary electric cells or storage cells connected to the terminals of the said bulb, a switch in the circuit of the said cells and the bulb, the switch being normally biassed to its circuit closing position and its actuating member normally protruding beyond the false bottom, so that when the vacuum flask is kept vertically on a table, stand, stool or the like, the said actuating member is pressed inwardly to open the said circuit.

A window is provided on the wall of the container or canister, against which the electric bulb is disposed. The actuating member of the said switch is biassed to its 'ON' position by means of a spring for example, a helical spring; alternately the movable contact member may be pivoted at its end remote from its operative end and loaded with a weight at its lower end. The spring or the weight will keep the movable contact member in its 'ON' or circuit closing position. The actuating member for example, a button, downwardly extending from the movable contact member is so disposed as to protrude normally from the lower end of the false bottom of

of the container or canister. When the flask is rested vertically on a flat horizontal surface the said buttom pressing on the surface is pushed inwardly to its 'OFF' or circuit open position. When the flask is lifted off its resting place, the movable contact member is restored to its 'ON' or circuit closed position by the spring or the loading weight so that the bulb is lighted. The flask can now be conveniently filled or emptied. When the flask is replaced, the light is put off as explained above.

My invention also includes a lighting or illuminating device, as described above, in a vacuum flask.

My invention is illustrated in the accompanying shcematic drawings, in which :-

Figure 1, shows a vacuum flask according to my invention resting on a supporrt ; only the false bottom being shown in section ;

Figure 2 shows the flask shown in figure 1, but lifted off its support ;

Figure 3 shows the flask without the lighting or illuminating device ;

Figure 4 shows the illuminating or the lighting device separately.

The flask shown in figures 1 to 3 has an outer container or canister 1 provided with the usual double walled glass bottle not shown, housed within it; the usual cup or cap secured to the container is shown at 2.

The container or canister 1 is formed with a false bottom (figure 1 to 3); the cylindrical and the top walls of the false bottom are shown at 3 and 4. An electric lighting or illuminating device L is housed in the said false bottom. The container or canister being generally cylindrical, the side wall 5 of the casing of the device L is also cylindrical; the top and the bottom of the said casing are marked 5A and 5B.

The device L has an electric idcandescent bulb 7 of say 2-5 volts, connected in the circuit of a source 6 of electrical energy for example, one or more primary or secondary (storage) cells; it is preferred to use dry storage cells of the larger type which are very compact and reliable. The electrical circuit of the source includes an electric switch the fixed and the movable contact arms and the fixed contacts of which are indicated by the numerals 8 and 9 and 8' and 9' respectively. The arm 9 is pivoted at 9A by means of a pin secured to the wall 5; the end of the arm 9 remote from the pivot 9A is provided with a downwardly extending button 10 which is biassed by a spring 10' to protrude below the lower wall 5B of the casing of the device L, through an aperture 5B' (figure 4), when the flask is held in hand. When the flask is placed vertically on a support 11 (Figure 1), the bottom 10 coming into contact with the support is pushed in against the force of the spring 10', so that the movable contact arm 9 is caused to lift the movable contact 9' away from the fixed contact 8', thereby interrupting or breaking the circuit of the source 6 and the bulb 7 (figure 2). When the flask is lifted off the support 11, the button 10 is again free to protrude through the aperture 5B' under the influence of the spring 10', so that the contact 9' is caused to bear on the contact 8', thereby completing or making the said electric circuit.

A window is provided against the bulb 7 by an aperture 3' in the cylindrical wall 3 and another aperture 5' in the cylindrical wall 5 of the casing of the device L. The said casing is so made as to be push-fitted within the wall 3 of the false bottom. When the casing is fitted in the false bottom, the apertures 3' and 5' are aligned so that when the flask is lifted the light from the bulb 7 passes through them.

In stead of providing a spring 10' the button 10 itself may be weighted or alternatively a piece W (as shown in dotted lines in figures 1, 2 and 4) of lead or other dense substance may be provided on the member 9; this weight W will serve the same function as the spring 10'.

If desired the device L can be removed from the false bottom of the flask and carried off and used as a pocket torch.

I CLAIM :-

1. A vacuum flask comprising an outer casing or canister having a false bottom in which is housed an electric lighting or illuminating device which consists of an electric incandescent bulb, one or more electric primary cells or storage cells connected to the terminals of the said bulb, a switch in the circuit of the said cells and the bulb, the switch being normally biassed to its circuit closing position and its actuating member normally protruding beyond the false bottom, so that when the vacuum flask is kept vertically on a table, stand, stool or the like, the said actuating member is pressed inwardly to open the said circuit.

2. A vacuum flask as claimed in claim 1, in which the said switch has a fixed contact arm, and a movable contact arm pivoted at one end and provided with the said actuating member and biassed downwardly to bring the movable contact against and in electrical contact with the fixed contact on the fixed contact arm.

3. A vacuum flask as claimed in claim 1 or claim 2, in which a spring for example, a helical spring is provided to bias the movable contact arm and the actuating member downwardly.

4. A vacuum flask as claimed in claim 1 or 2, in which a weight is provided to bias the actuating member to protrude beyond the false bottom.

5. A vacuum flask as claimed in any of the preceding claims, in which the lighting or illuminating device has a casing which is push-fitted in the said false bottom.

6. A vacuum flask as claimed in any of the preceding claims, in which a window is provided in the said false bottom against the said electric bulb.

7. A vacuum flask as claimed in claim 5, in which two apertures are provided on the side walls of the said false bottom and the casing of the lighting and illuminating device, the said apertures being aligned when the said casing is fitted in the false bottom, so as to provide a window opposite to the said bulb.

8. In a vacuum flask having an outer container or canister formed with a false bottom, an electric lighting or illuminating device comprising a casing adapted to be fitted into the false bottom, an electric incandescent bulb and one or more electric primary cells or storage cells and an electric switch connected together to form a circuit, and an actuating member for the switch, biassed to protrude normally beyond the said false bottom so as to make the switch and which is puthed inwardly when the vacuum flask is placed on support so as to break the switch.

9. A vacuum flask substantially as herein described and illustrated in the accompanying drawings.

ALIMAHOMED CHHAGANBHAI PADAMSEE
By P. S. PAI & CO,
Authorised Agents.

Dated this 18th day of October 1961.

Printed by The Nolys Printing Works, Calcutta 1.

ALIMAHOMED CHHAGANBHAI PADAMSEE
NO. 74725 OF 1960

ONE SHEET

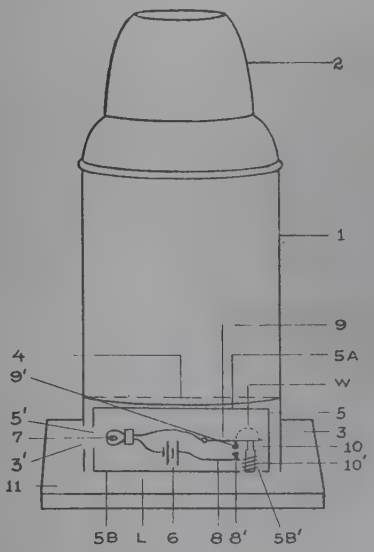
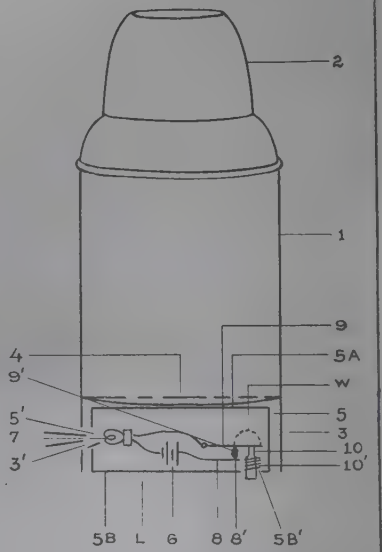


FIG. 1



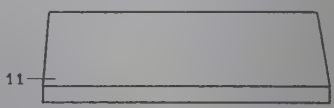


FIG. 2

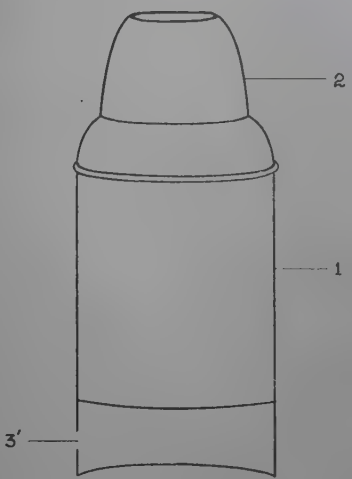


FIG. 3

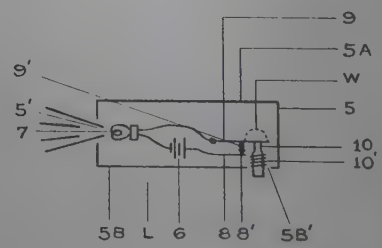


FIG. 4

for P. S. PAI & CO.,
APPLICANT'S AGENTS

REG. NO. 2273 E/44—106'58.

PRINTED AT THE SURVEY OF INDIA OFFICES. (P. L. O.)

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.
Specification No. 74726. Application No. 74726, dated 29th December 1960. Complete Specification left on 20th October 1961. (Application accepted 14th Deember 1961.)

PROVISIONAL SPECIFICATION

(Section 4)

" IMPROVEMETS IN OR RELATING TO A VACUUM FLASK OR LIKE CONTAINERS. "

ALIMAHOMED CHHAGANBHAI PADAMSEE, Indian National, C/o. Messrs. Salemahomed Padamsee and Company, 141, Sheriff Devji (Chuckla) Street, City of Bombay, State of Maharashtra, India.

The following Specification describes the nature of this invention :—

This invention relates to improvements in or relating to vacuum flask or like container which comprises of a bottle of glass provided within an outercanister or casing, and also with a handle portion, used for carring about or holding the while pouring out its contents.

When such flasks are used for containing beverages, especially a night-cap, they are often used during nights and at the bedside, where there is no adequate light for conveniently flash pouring out their contents.

It is the object of this invention to provide for a vacuum flask or the like container which is provided with a light within the body of its canister, and also with a switch in its handle portion, so that the light within the canister can be put on while using the vacuum flask, and put out when not required.

The canister of the vacuum flask according to this invention is provided with a false bottom into which storage batteries are contained. The electrical bulb may be provided, anywhere on the body of the canister, on its inside, preferably in the region near the mouth of the flask. That portion of the canister which comes against the said bulb is provided with a window. The said bulb is connected to the batteries provided in the false bottom of the canister through a spring loaded switch lever attached to the handle portion of the vacuum flask.

When the flask is lifted by its handle portion, the switch lever can be pressed simultaneously with the same grip, and the electrical circuit completed. The bulb near the mouthened of the flask glows and the contents of the flask can be easily poured out with the aid of the said light.

When the pressure on the said spring-level is released, such as when the flask is kept down, the circuit is automatically broken and the said bulb goes off.

The false bottom of the canister, containing the storage batteries, can be covered up with a suitable base plate, so that when so covered, nothing is externally visible.

ALIMAHOMED CHHAGANBHAI PADAMSEE
By P. S. PAI & CO.
Authorised Agents.

Dated this 26th day of December 1960.

COMPLETE SPECIFICATION

(Section 4)

Specification No. 74726.

" IMPROVEMETS IN OR RELATING TO A VACUUM FLASK OR LIKE CONTAINERS. "

ALIMAHOMED CHHAGANBHAI PADAMSEE, Indian National, C/o. Messrs. Salemahomed Padamsee and Company, 141 Sheriff Devji (Chuckla) Street, City of Bombay, State of Maharashtra, India.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This invention relates to vacuum flasks or like containers of the kind comprising of double walled glass bottles housed in outer casings or canisters having handles for carrying them about or holding them while pouring off their contents.

These flasks, as is well known, are used for keeping hot or cold beverages at elevated or sub-ambient temperatures respectively. They are particularly useful for keeping at hand night caps (beverages for use at night) as well as liquid foods for patients. If the contents of such flasks are to be poured off for use at nights the patients and/or others sleeping nearby, are likely to be disturbed by the switching on of the lights for this purpose.

The object of my invention is to provide vacuum flasks of the kind mentioned above with a simple and reliable electric lighting or illuminating device which will help emptying or filling of such flasks, without causing, any disturbance to the patient or other persons.

A vacuum flask of the kind described, according to my invention comprises a false bottom provided in the outer casing or canister, an electric lighting or illuminating device consisting of an electric incandescent bulb located with in the outer casing or canister and opposite to an aperture formed in the wall of the said casing or canister, one or more electric primary or secondary cells housed in the said false bottom, an electric circuit including the said bulb, the said cells and electric switch, and insulated electric conductors connected therebetween ; the said switch consisting of a fixed contact provided on the inner side of the handle of the outer casing or canister, a movable contact provided on an arm secured to the inner side of the said handle and normally biassed to keep the movable contact away from the fixed contact and adapted to bring the said contacts together when the same along with the said handle are gripped together by hand, so as to complete the said electric circuit.

The said electric cells are housed in a casing which is push-fitted within the false bottom in the outer casing or canister ; the insulated conductors connected to the terminals are led to the said bulb and the movable contact arm through apertures in the upper wall of the false bottom and the

clearance between the vacuum glass bottle and the outer casing or canister ; the conductor connecting the bulb and the fixed contact also being led through the said clearance and through the handle.

The movable contact arm does not need a spring or other biassing means to keep it away from the handle of the outer casing or canister ; as this arm is pivoted at its top end, it will, under the influence of its own weight keep the movable contact away from the fixed contact. Alternatively, the movable contact arm may be constituted by a spring blade anchored at its upper end into the said handle and acting under its own bias. If desired, however, a helical spring or other known forms of springs may be provided on the handle to keep the movable contact arm away from it.

A vacuum flask according to my invention is illustrated in the accompanying schematic drawings in which :

Figure 1 shows the flask in elevation, only the handle being shown in section and the inner details of the flask in dotted lines and,

Figure 2 shows the flask with the switch in its actuated position, the hand gripping the handle together with the movable contact arm not being shown.

The vacuum flask (figure 1) has an outer casing or canister 1, the usual double walled glass bottle 2 housed within its, a neck 1' secured to the top of the canister, a stopper 4 for the mouth of the bottle and a cup or cap 3 secured to the neck. The canister or casing is provided with a handle 1A. The canister or casing 1 has a false bottom ; a disc shaped casing 16 having a cylindrical wall 5 and top and bottom walls 7 and 6 can be push-fitted into the false bottom. One or more cells, 8, primary or storage, and located in the said casing. Two insulated conductors or lead in wires 9 and 10 connected to the opposite poles or terminals of the cell or cells 8 are led through apertures in the top wall 7 of the said casing 16 in the false bottom, and the bottom wall of the casing or canister 1, upwardly through clearance space between the bottle 2 and the outer casing or canister 1, to and electric bulb 15 provided near the upper end of the casing or canister 1 and to a movable contact arm 12. The arm 12 may be a blade of metal sheet pivoted at its upper end to the handle 1A or a metallic spring blade anchored at its upper and into the handle 1A on its inner side. The arm 12 has a movable contact 14 secured to it in electrically conducting relationship. The fixed contact 13 of the switch is secured to the handle 1A on its innerside and opposite to the movable contact 14. An insulated conductor or lead in wire 10A connects one terminal of the bulb 15 to the fixed contact 13.

When the flask is lifted by gripping the handle 1A together with the movable contact arm 12, the latter is moved towards the handle bringing the movable contact 14 into engagement with the fixed contact 13, thereby making or the completing the electric circuit. The bulb 15 is now lighted ; light from the bulb passing to the outside through aperture 11 in the canister 1 illuminates the outside so that the contents of the glass bottle can be poured of conveniently after the cup 3 and the stopper 4 are removed. The hand gripping the handle 1A and the movable contact arm 12 is as shown in figure 2 for the sake of clarity. When the flask is set down on a support for example, a table, or stool and the arm 12 released the circuit is broken by the arm moving away from the handle 1A.

I CLAIM :—

1. A vacuum flask of the kind described comprising a false bottom provided in the inner casing or canister, an electric lighting or illuminating device consisting of an electric incandescent bulb located within the outer casing or canister and opposite to an aperture formed in the wall of the said casing or canister, one or more electric primary or secondary cells housed in the said false bottom, an electric circuit including the said bulb, the said cells, an electric switch, and insulated electric conductors connected therebetween ; the said switch consisting of a fixed contact provided on the inner side of the handle of the outer casing or canister, a moavble contact provided on an arm secured to the inner side of the said handle and normally biassed to keep the movable contact away from the fixed contact and adapted to bring said contacts together when the same along with the handle are gripped together by the hand, so as to complete the said circuit.

2. A vacuum flask as claimed in claim 2, in which the said movable contact arm is a spring blade anchored at its upper end into the handle and having the movable contact provided thereon in an electrically conductive relationship.

3. A vacuum flask as claimed in claim 1, in which the movable contact arm is a piece of metal sheet pivoted at its upper end to the said handle and normally hanging freely under its own weight and away from the handle.

4. A vacuum flask according to any of preceding claims, in which the said electric cell or cells are housed in a casing which is adapted to be push-fitted into the said false bottom.

5. A vacuum flask as claimed in any of the preceding claims, in which the said electric conductors from the terminals of the cells or cell are led to the said bulb and the movable contact arm through apertures in the top wall of the casing in the false bottom and through the clearance between the glass bottle and the outer casing or canister and the lead from the said bulb to the fixed contact also being led through the said clearance.

6. A vacuum flask substantially as herein described and illustrated in the accompanying drawings.

ALIMAHOMED CHHAGANBHAI PADAMSEE
By P. S. PAI & Co.
Authorised Agents.

Dated this 18th day of October 1961.

Printed by The Nalys Printing Works, Calcutta-1.

...LIMAHOMED CHHAGANBHAI PADAMSEE
NO. 74726 OF 1960

ONE SHEET

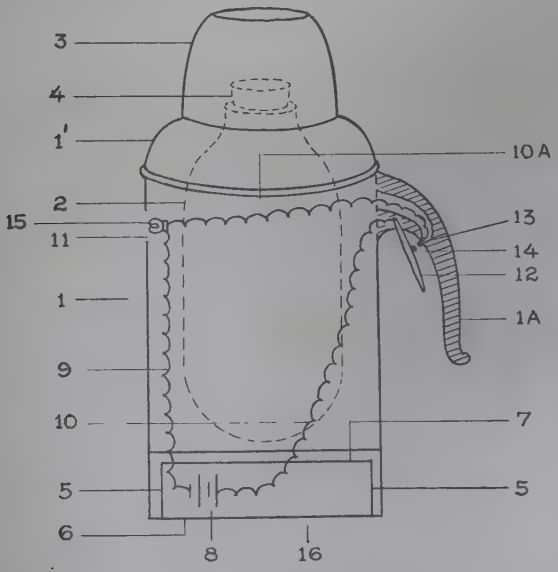


FIG. 1

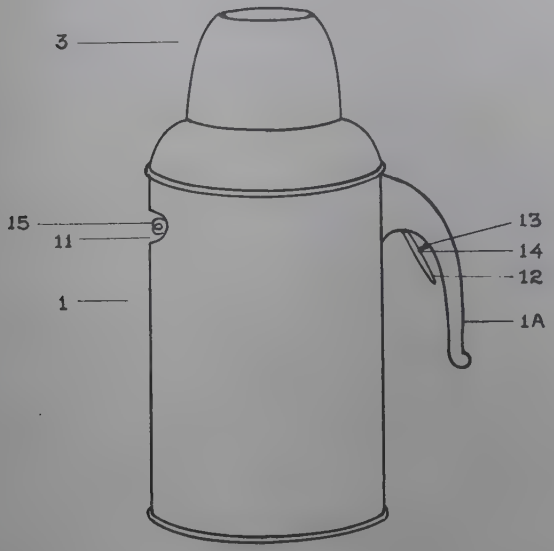


FIG. 2

for P. S. PAI & CO.,
APPLICANT'S AGENTS

REG. NO. 2273 E/44—100'58.

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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

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STABILISED POLYMERIC COMPOSITIONS.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, MANUFACTURERS, OF IMPERIAL CHEMICAL HOUSE, MILLBANK, LONDON, S.W.1, ENGLAND, A BRITISH COMPANY.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to stabilised polymeric compositions. It is well-known that it is desirable to incorporate antioxidants into solid polymers and predominantly hydrocarbon copolymers of unsaturated hydrocarbons *e.g.*, polyethene (the solid polymers of ethylene) polypropylene, polyisobutylene, polybutene-1, poly-3-methyl-butene-1, poly-4-methyl-pentene-1, ethylene-propylene copolymers, and the polymers and copolymers of conjugated dienes, for instance butadiene and isoprene, *e.g.*, natural rubber, polybutadienes, polyisoprenes, and copolymers of butadiene with minor amounts of styrene, acrylonitrile or methyl methacrylate. These polymers, hereinafter and in the appended claims, will be referred to as solid olefine polymers as hereinbefore defined.

Solid isotactic aliphatic mono-α-olefine polymers, by which we mean polymers not less than 75 per cent. of which are insoluble in heptane, particularly isotactic polypropylene, are materials with excellent mechanical and electrical properties which may be shaped for example into sheets, tubes, films, filaments and mouldings by the shaping processes of the plastic industry. Becuase of their generally high melting points, however, it is necessary to use particularly active stabilisers in order to protect these polymers againt degradation at elevated temperatures in processing or in subsequent use.

It is an object of the present invention to provide improved stabiliser compositions and solid olefine polymer compositions particularly solid isotactic mono-α-olefine polymer compositions usefully stabilised therewith.

Most of the previous proposals have been for the use of amines. phenolic compounds or sulphur compounds as antioxidants.

In our Indian Patent Applications Nos. 72649 and 79282 we show that when certain types of phenolic condensate are used in combination with diesters, or N N'-di- or N,N,N',N' tetra hydrocarbon-substituted diamides of thiodialkanoic acids (conjointly referred to hereinafter as thiodialkanoic acid derivatives) the most remarkable synergistic stabilisation of solid olefine polymer is obtained.

In the work which led to the filing of the above mentioned applications many combinations were examined which exhibited no significant synergism. For example, in polythene compositions, bisphenol A, tetrachloro bisphenol A, ethylidene bisphenol, or chromans formed by the condensation of m- or p-cresol with acetone, and Dianin's compound (a condensate of phenol with mesityl oxide) show no appreciable synergism with dilauryl thiodipropionate when the compounds are used at concentrations of 0.1 per cent. by weight of the composition.

Similarly in polypropylene compositions there is no appreciable synergism between 2,4-didodecyl phenol and dilauryl thiodipropionate (both compounds at 0.5 per cent. by weight of the composition).

Turning now to compositions comprising combinations of different sulphur compounds with the same phenolic compound in polyethene (the compounds being used at concentrations of 0.1 per cent. by weight of the composition) dilauryl sulphide, 2,6-diphenyl tetrahydrothiopyrone and ethyl β-benzoylethyl sulphide show no appreciable synergism with a condensate of three molecules of 3-methyl-6-tertiary butyl phenol with one molecule of crotonaldehyde.

If however, a combination of dilauryl thiodipropionate and the above crotonaldehyde condensate is tested (the compounds being used at concentrations of 0.1 per cent. by weight of the polythene composition or 0.5 per cent. by weight of the polypropylene composition) a most astonishing degree of synergism is displayed.

From these results it is plain that an improved stabilising action is not in general to be expected from combinations of phenolic compounds and sulphur compounds.

It has previously been proposed to use hydroxyspirohydrindenes as sole antioxidants for rubber.

According to the present invention we now provide a composition which is surprisingly effective for stabilising olefine polymers as hereinbefore defined and comprises a solid polymer or copolymer of an aliphatic mono-α-olefine, natural rubber, or a solid polymer or copolymer of a conjugated diene, a diester of β-thiodipropionic acid and a hydroxyspirohydrindene having the formula as shown in the accompaying drawing, in which R_1 and R'_1 are -R or -OR or -OH radicals in which -R is a hydrocarbon radical and R_2, R_3, R'_2, and R'_3 may be -R, -OR or -H radicals, R_4 and R'_4 may be R or H radicals and R_1, R_2, R_3 R_4, R'_1, R'_2, R'_3 and R'_4 may be the same or different

It will be understood from the well-known mechanisms of the chemical reactions used in the preparation of our hydroxyspirohydrindenes that their hydroxyl groups will be in positions 5 or 6 and 5' or 6', normally in positions 5 and 5'.

In a modification of this invention hydrocarbon groups or chlorine or bromine atoms may be introduced into a hydroxyspirohydrindene of lower molecular weight—which may already have substituents—by for example the methods disclosed hereinafter.

We believe that in this case the substituents are introduced into positions adjacent to the phenolic hydroxyl group. This is borne out by the fact that the infra-red spectrum of 2-tertiary butyl phenol/acetone condensate is almost indistinguishable from that of a condensate of phenol and acetone which has been butylated after its formation.

Whilst we find that usefully stabilised polyolefine compositions may be obtained with widely varying ratios of said thiodialkanoic acid derivatives to said dihydroxyspirohydrindene and whilst our invention is in no way limited to particular ratios of these ingredients, we find that particularly effective ratios of these ingredients are when there are from 1 to 10 hydroxyl radicals provided to the composition by the dihydroxyspirohydrindene to each sulphur atom provided to the composition by the thiodialkanoic acid derivative. The content of these components in polyolefine compositions may also be varied over very wide limits. Thus, polyolefine compositions useful for a wide variety of applications, *e.g.*, for making films, are effectively stabilised with, for example, 40 parts by weight per million (0.004 per cent.) of the dihydroxyspirohydrindene, alongwith the thiodialkanoic acid derivative. For polyolefines which are more susceptible to oxidation than polythene or for polyolefine compositions which are to be subjected to vigorous conditions of oxidation during their processing or during their later use larger amounts of these additives would be used. In general with polythene it is sufficient to use from 0.004 to 0.5 per cent. by weight of the dihydroxyspirohydrindene and normally from 0.004 to 0.15 per cent. by weight of the dihydroxyspirohydrindene. For compositions of polypropylene, rubber or polymers or copolymers of conjugated dienes larger amounts of the components are usefully used. It is usually sufficient to use upto 5 per cent. by weight of the dihydroxyspirohydrindene together with the thiodialkanoic acid derivative and, in general, up to 0.5 per cent. is sufficient.

Any diester or N,N'-di- or N,N,N',N'-tetra hydrocarbon substituted diamide of a thiodialkanoic acid may

be used in the compositions of this invention. We find, however, that particularly satisfactory compositions are obtained when the derivatives are esters of aliphatic alcohols, especially those of alcohols of 10 to 20 carbon atoms, *e.g.*, those of lauryl or stearyl alcohol, and of thiodiglycollic, thiodipropionic or thiodibutyric acids.

The hydrocarbon groups in the hydrocarbon-substituted diamides are preferably alkyl groups, particularly those corresponding to the preferred alcohols mentioned above. In general, for the same number of total carbon atoms in the alkyl groups, a disubstituted diamide is preferred to a tetra-substituted diamide of a given thiodialkanoic acid.

The dihydroxyspirohydrindene may for example be produced by condensing a phenol having a free meta and para position with a ketone having at least 2 free hydrogen atoms on each of the carbon atoms directly attached to the carbonyl group under conditions in which three molecules of the ketone condense with two molecules of the phenol. Preferably the substituents R_1, R_2 and R_3, or R'_1, R'_2 and R'_3 of the phenol do not together provide more than twelve additional atoms of atomic weight of twelve or greater to each phenolic nucleus. Suitable conditions are for example provided by carrying out the reaction in the presence of large quantities of a mixture of glacial acetic acid and concentrated hydrochloric acid as is described by Baker and Besley (J. C. S. (1939) p. 1421-4). Mono-substituted phenols having the substituent in the ortho position condense most readily. Acetone, methyl ethyl ketone and diethyl ketone also condense readily.

The reaction product is preferably purified before use, for example, by distillation in high vacuum or in the manner described by Baker and Besley. The crude dihydroxyspirohydrindene separated from the reaction medium may however also be used. Suitable phenols are, for example, ortho cresol, guaiacol, catechol, pyrogallol, 2,6-dimethyl phenol, 2-isopropyl phenol, 2-tertiary butyl phenol, 2-octyl phenol, 2-nonyl phenol, 2-decyl phenol, 2-methyl-6-isopropyl phenol, 2-methyl-3-tertiary butyl phenol, 2-methyl-6-tertiary butyl phenol, and 2-methyl-6-octyl phenol. Hydrocarbon substituents may be introduced into a hydroxyspirohydrindene having free reactive positions, *e.g.*, a condensate of two molecules of phenol with three molecules of acetone, by reacting the hydroxyspirohydrindene with, *e.g.*, butens, pentenes, hexenes, heptenes, octenes, nonenes, decenes, undecenes, or dodecenes or the corresponding alcohols or halides which may be commercial technical grade mixtures or with styrenes or cyclohexenes in the presence of a catalyst. The hydroxyspirohydrindenes may also if desired be subjected to chlorination or bromination although this does not usually increase their activity. The stabilised compositions of this invention may be prepared in a variety of ways depending on the nature of the solid olefine polymer on the manner in which it is produced and also on the amount of stabilising maetrial to be incorporated in the compositions. If only a small amount of antioxidant, *e.g.*, 40 parts per million of each component is to be incorporated into polythene made by the high pressure process the stabilising components are conveniently incorporated by dissolving them in a high boiling hydrocarbon liquid and this solution is mixed with the hot polythene in a suitable container after the polythene issues from the converter in which it is produced. Larger quantities of the stabilising components may be mixed with a solid olefine polymer by any of the mastication processes. A satisfactory method for mixing the stabilising ingredients with a solid olefine polymer made by the low pressure process is to add a solution of the components to the olefine polymer powder obtained by this process and then to remove the solvent for the stabilising component by evaporation.

The stabilising ingredients of this invention may be mixed with latices of natural rubber or the polymers or copolymers of conjugated dienes by forming dispersions of these in water mixing these dispersions with the latices to be stabilised, and if desired, coagulating or drying the latex compositions.

The compositions of this invention may also contain other stabilisers such as material which absorb ultra violet light. They may also contain further ancillary ingredients such as processing aids, for example, the soaps of calcium and zinc and also such materials as pigments, dyes and fillers, and when necessary the other ingredient compounded with rubbers, *e.g.*, vulcanising ingredients. Thus, carbon black may be incorporated either as an absorber of ultra violet light, as a filler or as a pigment.

The following experimental details illustrate our invention. It will be understood, however, that our invention is in no way limited by these details.

PREPARATIONS.

1. Guaiacol (200 g), acetone (190 ml), acetic acid (400 ml) and concentrated hydrochloric acid (320 ml) were heated under reflux on a steam bath for 110 hrs. The crystalline material was filtered off, after the mixture had cooled and stood for a few hours, and washed thoroughly with cold acetic acid and water and dried. The product (30 g) was recrystallised from alcohol in a Soxhlet extractor.

M.pt. 266-7°C.; after further recrystallisation (yield 23.9 g) m.pt. 268-9°C.

Analysis	*Found %*	*Required by $C_{28}H_{28}O_4$*
C	74.7	75.0
H	7·9	7.7

2. A mixture of o-cresol (100 g), acetic acid (250 ml) acetone (75 ml) and concentrated hydrochloric acid (190 ml) was heated under reflux on a steam bath for 60 hours, and then stirred into water. The very thick mass was collected, washed by kneading under water, dried by heating under diminished pressure on the water bath. The residue was then fractionated by vacuum distillation. The main fraction (b.p. 220-240°/0.3 mm) was recrystallised from xylene to give small crystals, m.p. 245-7°C.

3. 2.6 Xylene-1-ol (110 g), acetic acid (250 ml), acetone (75 ml) and concentrated hydrochloric acid were heated under reflux on a steam bath for 65 hours. The mixture was cooled, and water was added. The top layer was collected, washed successively with water, sodium carbonate solution, and water, and dried by distilling under vacuum on a water bath.

The gummy material was fractionated by vacuum distillation. The main fraction (b.p. 220-230°C./1.3 mm) was yellow and because crystalline on standing. No suitable recrystallisation solvent could be found.

The brittle gum was acetylated with acetic anhydride and sodium acetate and the crude product was recrystallised from ethanol. m.pt. 230-235°C.

The acetate was hydrolysed and the crystals obtained on acidification were dried and recrystallised from xylene. m.pt. 194-195.5°C.

Analysis	*Found %*	*Required for $C_{28}H_{32}O_2$*
C	82.0	82.4
H	8.9	8.9
		Required for $C_{28}H_{31}O_4$
(Acetate) C	76.8	77.6
H	8.0	8.1
Equivalent	*Found*	*Expected.*
(Saponification of Acetate)	229	224.3

These are believed to be new compounds.

4. Catechol and acetone were condensed by the method of Baker (J. C. S.) (1934) p. 1678). Some of the product was brominated, as described by Baker, and a further portion was chlorinated by the following method:—

A solution of the condensate (3 g) in glacial acetic acid was saturated with chlorine. A bright red precipitate was formed. Sodium sulphite was added, and the mixture allowed to stand until the red colour had disappeared. The resulting light brown precipitate was filtered, recrystallised from dilute acetic

acid, and dried in a vacuum desiccator. Analysis for chlorine (found —25 per cent.) indicated the presence of about 83 per cent. of the theoretical maximum substitution.

5. Catechol (132 g), methyl ethyl ketone (118.8 g) glacial acetic acid (300 ml) and concentrated hydrochloric acid (240 ml) were heated on a steam bath for 48 hours. A heavy crystalline mass formed. The reaction mixture was allowed to cool and the crystals were filtered off and recrystallised several times from glacial acetic acid. The still discoloured crystals were dissolved in the minimum amount of boiling ethanol, activated charcoal was added and the solution was filtered hot. An equal volume of boiling glacial acetic acid was added to the hot filtrate. The colourless crystals deposited on standing were filtered, dried under high vacuum over solid potassium hyroxide and finally in a drying pistol at 100°C. over solid potassium hydroxide and under high vacuum.

The product melted with decomposition at 302-5°C.

The acetate was prepared and recrystallised from ethanol, m. pt. 169-173°C.

Analysis of acetate	*Found %*	*Required for $C_{32}H_{36}O_8$*
C	79.3	69.8
H	7.1	7.0
O	22.4	23.2

This compound is described by Fabinyi and Szeky (Ber. *38*, 2307).

6. Pyrogallol and acetone were condensed by the method of Baker and Besley (J. C. S. *1939* p. 195).

7. The condensation of phenol and acetone was described by von Braun in 1929 (Liebigs Annalen 472, p. 65), but the product was not recognised at the time to be a spirohydrindene. This was shown by Curtis (Chem. and Ind. (1960) p. 928).

Octylated, styrenated, and methylcyclohexenated phenol/acetone condensates were prepared as follows:

7a. The phenol-acetone spirohydrindene (5.1 g) and concentrated sulphuric acid (0.5 g) were placed in a flask and sufficient toluene added to dissolve the solid at 100°C. Octene (2,4.4-trimethyl pentene-1, 3.8 g) in toluene (20 ml) was added slowly and the mixture refluxed and stirred for 6 hours.

The reaction mixture was then cooled, washed with water, with sodium carbonate solution, and finally with water again. The toluene solution was dried over anhydrous sodium sulphate and the toluene removed by evaporation.

The residue was then distilled *in vacuo*.

A fraction of b.p. 210-220°C./0.1 mm and the residue were tested as antioxidants.

7b. The styrenated product was prepared as in (a), replacing the octene by styrene (3.5 g) and using 30 ml of toluene.

A fraction of b.p. 210-220°C./0.1 mm and the residue were tested as antioxidants.

7c. The spirohydrindene (10.3 g), methylcyclohexene (11.1 g) and a 50 per cent. solution of concentratetd sulphuric acid and glacial acetic acid (6 ml), were heated on the steam bath for 6 hours, the mixture cooled, toluene added and the product worked up as before.

The residue, after vacuum distillation to remove unchanged starting materials, was tested as an antioxidant.

8. Diethyl ketone (86.2 g 1.0 mole) catechol (55.1 g 0.5 mole) glacial acetic acid (150 ml) and concentrated hydrochloric acid (100 ml) were heated on the steam bath for 5 days. On cooling, crystals were deposited in the flask and these were filtered, washed with cold acetic acid and recrystallised by dissolving in the minimum amount of ethanol, an equal volume of boiling acetic acid being added to the solution.

The white crystals were filtered, sucked dry and placed in a drying pistol under high vacuum at 150°C.

Analysis	*Found%*	*Required for $C_{27}H_{36}O_4$*
C	76.6	76.4
H	8.6	8.6

The product melted above 300°C. with decomposition, beginning to char at 280°C.

This compound is described by Fabinyi and Szeky (Ber. *38*, 2307).

9. 2-tertiary butyl phenol (75 g), acetone (40 ml), glacial acetic acid (125 ml), and concentrated hydrochloric acid (100 ml) were heated on the steam bath for 60 hours. The dark, viscous reaction mixture was washed with cold water and the thick oily organic layer separated by decantation, washed several times with hot water while stirring vigorously and finally dried by heating on the steam bath under reduced pressure. On cooling the gum became a brittle solid, which was fractionated by vacuum distillation.

The main fraction (b.p. 190-206°C./1.0 mm) distilled as a thick heavy yellow liquid which became brittle on cooling.

Attempts to crystallise this solid directly were unsuccessful.

The acetate (B) was prepared in the usual manner, and recrystallised from ethanol. m. pt. 235-237°C.

The recrystallised acetate was hydrolysed and the white crystals (A) were recrystallised from xylene. m. pt. 135°C.

Analysis	*Found %*	*Required for $C_{29}H_{40}O_2$*	
C	82.6	82.8	(A)
H	9.7	9.6	
		Required for $C_{33}H_{44}O_4$	
C	78.6	78.5	(B)
H	8.8	8.8	

The equivalent (by saponification of the acetate) was 240, the expected value corresponding to the above formula being 252.

These are believed to be new compounds. A compound showing substantially the same infra-red spectrum as (A) was obtained by butylation of the phenol/acetone spirohydrindene of preparation 7.

The infra-red spectra of preparations 1 to 9 indicated the presence of benzene rings substituted to a degree consistent with the spirohydrindene structure in each case.

EXAMPLE 1.

Polythene of melt flow index 2 (as measured by the A.S.T.M. method) was mixed with various thiodialkanoic acid derivatives and various hydroxyspirohydrindenes including some derivatives of hydroxyspirohydrindenes formed by chlorination, bromination, or reaction with styrene, octene or methylcyclohexene of a preformed hydroxyspirohydrindene, as set out in Table 1 below (the quantities shown being per cent. by weight of the polythene composition), by milling these ingredients together at 140°C. The compositions produced were pressed at 150°C. into sheets 1/200th of an inch thick. Small samples of the 1/200th of an inch pressing were placed on glass wool in a glass bulb which contained some Type 5A "Linde" (Registered Trade Mark) molecular sieves to absorb gaseous products of oxidation and which was connected by a U-tube containing mercury to another glass bulb. ("Linde" molecular sieves are synthetic zeolites produced and sold by Union Carbide and Carbon Corporation). Both bulbs were filled with air, then sealed and the apparatus placed in a vapour thermostat at 140°C. Movement of the mercury indicated oxidation of the polythene and the time in the vapour thermostat at 140°C. until a notable rate of movement of the mercury was apparent was measured. Samples of an inch long by ¼ of an inch wide cut from the 1/200th of an inch thick sheet were placed on microscope slides in an air oven at 140°C. Samples were removed at intervals and the extent of oxidation was estimated by measuring carbonyl group concentration by infra-red spectroscopy using the absorption band at 5.85 microns wave length. The time before the oxygen present as carbonyl was greater than 0.1 per cent. was measured.

condensates used was less than was used with polypropylene, the staining was inappreciable.

In the antioxidant combinations of our above-mentioned copending British Patent Applications, for the best results the phenol or the aldehyde or ketone, condensed to form the phenolic compound preferably both, should have a large substituent, *e.g.*, a large hydrocarbon substituent.

It is, therefore, in the highest degree surprising that we now find as will be seen from Examples 1 to 4 that although the phenol must have a substituent, the smaller substituents, *e.g.*, methyl, methoxy, hydroxy are of the same order of effectiveness as the larger substituents, *e.g.*, octyl or nonyl groups in both polythene and polypropylene.

We prefer that the substituents in the phenolic nuclei do not together provide more than twelve additional atoms of atomic weight twelve or greater to each phenolic nucleus as the hydroxyspirohydrindenes of high molecular weight, in general are not more useful but merely more expensive.

As will be seen from the foregoing Examples, two sets of experiments have been carried out with polythene.

In the first set, the stabilised compositions are aged in an enclosed vessel and the oxygen uptake at 140°C. measured volumetrically; under these conditions the volatility of the stabiliser components has little effect on the measurements, and the test is an indication of the behaviour in service of the stabilised compositions under conditions such that loss of stabiliser by volatilisation is unimportant.

In this test we find that there is little to choose between the condensates having small substituents, *e.g.*, 2,6-dimethyl phenol, guaiacol and catechol, and those having large substituents, *e.g.*, the octylated, styrenated and t-butylated condensates.

In the second set, the stabilised compositions are aged in an oven at 140°C. the increase in carbonyl oxygen being followed by measuring the infra-red absorption at 5.85 microns in samples removed at intervals. This test takes into account the volatility of the stabiliser components and is a measure of he behaviour of the compositions in processing or subsequent use when the stabiliser may volatilise, *e.g.*, at high temperatures.

In this test, the condensates having large hydrocarbon substituents and the catechol and pyrogallol condensates are for the most part roughly equivalent; especially good results are obtained with the catechol/acetone condensate, the condensates of o-cresol, guaiacol, and 2,6-dimethyl phenol being less satisfactory.

In the polypropylene embrittlement test in which the polypropylene samples are held in an air oven at 140°C. until they are found to be brittle, the catechol/diethyl ketone condensate is outstanding. The other condensates tested show no very significant differences, except for the guaiacol/acetone condensate which is slightly less active.

Chlorination or bromination of the condensates generally does not improve or even reduces their activity in the above tests. On the basis of the results, on the grounds of their great activity, we prefer the pyrogallol condensates for stabilising polythene which is not to be exposed to extremes of temperature in subsequent use and in cases in which the somewhat greater level of staining caused by these condensates is not a disadvantage, *e.g.*, in dark coloured, for instance carbon-black filled compositions.

For use in lighter coloured compositions any of the other condensates shown may be used, whilst if it is particularly important to avoid staining the hydrocarbon-substituted condensates are preferred.

The choice in this case will be principally determined by the cost and availability of starting materials and the ease of carrying out the condensation; condensates of o-cresol are particularly preferred for reasons of economy.

For stabilising polythene which is to be exposed to high temperatures in subsequent use we prefer the catechol, pyrogallol and t-butyl phenol condensates, and the methylcyclohexenated phenol condensates. The remarks as to staining apply here also.

For stabilising polypropylene we prefer the catechol/diethyl ketone condensate for its effectiveness, and condensates of o-cresol for reasons of economy.

We claim:

1. A polymeric composition comprising a solid polymer or copolymer of an aliphatic mono-α-olefine, natural rubber, or a solid polymer or coplymer of a conjugated diene, a diester of β-thiodipropionic acid and a hydroxyspirohydrindene having the formula as shown in the accompanying drawing, in which R_1 and R'_1 are -R or -OR or -OH radicals in which -R is a hydrocarbon radical and R_2, R_3, R'_2 and R'_3 may be -R, -OR or -H radicals, R_4 and R'_4 may be R or H radicals and R_1, R_2, R_3, R_4, R'_1, R'_2, R'_3 and R'_4 may be the same or different.

2. A composition according to Claim 1 in which the diester of β-thiodipropionic acid is an ester of an aliphatic alcohol having from 10 to 20 carbon atoms.

3. A compositon according to Claim 2 in which the alcohol is lauryl or stearyl alcohol.

4. A compositon according to any of the preceding claims in which the substituents R_1, R_2 and R_3, or R'_1, R'_2 and R'_3 of the phenol do not together provide more than twelve additional atoms of atomic weight of twelve or greater to each phenolic nucleus.

5. A composition according to any of the preceding claims in which the hydroxyspirohydrindene is the product of condensation of two molecules of a phenol with three molecules of a ketone.

6. A composition according to Claim 5 in which the ketone is an aliphatic ketone.

7. A composition according to Claim 6 in which the ketone is acetone or methyl ethyl ketone.

8. A composition according to any of Claims 5 to 7 in which the phenol is 2,6-dimethyl phenol.

9. A composition according to any of Claims 5 to 7 in which the phenol is catechol.

10. A composition according to any of Claims 5 to 7 in which the phenol is o-cresol.

11. A composition according to any of the preceding claims in which there are from 1 to 10 hydroxyl radicals provided to the composition by the hydroxyspirohydrindene to each sulphur atom provided to the composition by the diester of β-thiodipropionic acid.

12. A polymeric composition according to the preceding claims in which the weight of hydroxyspirohydrindene is from 0.004 to 5 per cent. by weight of the composition.

13. A polymeric composition according to Claim 12 in which the solid polymer is a solid polymer of ethylene and the weight of hydroxyspirohydrindene is from 0.004 to 0.5 per cent. by weight of the composition.

14. A polymeric composition according to Claim 13 in which the weight of hydroxyspirohydrindene is from 0.004 to 0.15 per cent. by weight of the composition.

15. A polymeric composition according to Claim 12 in which the solid polymer is a solid polymer of an olefine having at least three carbon atoms and the weight of the hydroxyspirohydrindene is up to 5 per cent. by weight of the composition.

16. A polymeric composition according to Claim 15 in which the weight of hydroxyspirohydrindene is up to 0.5 per cent. by weight of the composition.

17. A polymeric composition according to any of Claims 12, 15 and 16 in which the solid olefine polymer is polypropylene.

18. A composition according to Claim 1 substantially as hereinbefore defined with particular reference to experiment 9.11 of Table 1 and 8.1 of Table 2.

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Dated this 29th day of December 1960.

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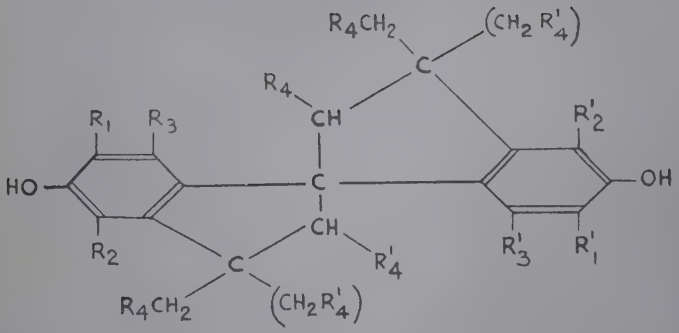
IMPERIAL CHEMICAL INDUSTRIES LIMITED.
NO. 74727 of 1960.

(1 Sheet)



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(Accepted 2nd May 1962.)

LUBRICATING COMPOSITION.

SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N. V., a Netherlands Corporation, at 30, Carel van Bylandtlaan, The Hague, The Netherlands.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to hydrocarbon lubricating oil compositions and particularly to engine lubricants having an improved viscosity index and having improved wear inhibition and detergency, as well as enhanced oxidation and corrosion inhibition.

Until recently, lubricants were commonly improved by adding various oil-soluble metal salts such as polyvalent metal sulphonates, carboxylates, phenates, phosphates or thiocarbamates. Some of these substances, such as the sulphonates, phenates and carboxylates possess detergent properties, some such as thiocarbamates are useful because of their corrosion inhibiting properties and some such as the phosphates are useful as antioxidants. In general these metallic compounds, when subjected to high temperature and high pressure conditions, break down and even act as pro-oxidants, causing deterioration of the oil base resulting in corrosivity, wear, etc. Recently certain non-ash forming oxygen and/or nitrogen-containing polymeric additives have been introduced as oil additives, but these generally lack wear inhibiting and extreme pressure properties as well as good high temperature oxidation inhibiting properties. Attempts to impart these properties to oils containing non-ash forming polymeric detergents by addition of conventional anti-wear and extreme pressure agents have been unsuccessful since generally they tend to form complexes which cause sludging and instability of the composition.

Also, certain types of non-ash oil additives such as copolymers of polymerizable monomers containing a basic alkyl amino group and acrylate esters, *e.g.*, copolymers of dodecyl methacrylate/diethylaminoethyl-methacrylate (PI.164 manufactured and sold by E. I. duPont) have been incorporated in lubricants to combat various forms of abnormal combustion in high-compression engines and to provide protection against scuffing, surface ignition characteristics (pounding, preignition, piston burning and wild ping) and improvement in octane requirement increase. However, in some of these respects compounded lubricants of this type have not met up to expectation particularly with respect to scuffing protection so that it has been necessary to introduce ash forming additives such as certain metal salts, *e.g.*, zinc thiophosphates to overcome this defect. This in turn however has been the cause of preignition problems and high-temperature instability even if such compounded lubricants contain certain well known anti-oxidants of the phenolic or aromatic amine type, *e.g.*, 2,2-di (p-hydroxyphenol) propane, 2,6-ditert-butyl-4-methylphenol, phenyl-alpha-naphthylamine and alpha-naphthylamine.

It has now been discovered that a combination of two particular classes of non-ash forming lubricant additives is unexpectedly effective in improving hydrocarbon lubricants with respect to wear inhibition, scuffing, detergency, storage stability, oxidation stability, colour stability and inhibiting pounding wild ping, valve burning and the like.

The invention relates to improved hydrocarbon lubricating oil compositions comprising a major proportion of a hydrocarbon lubricating oil and minor proportions of an oil-soluble copolymer of (1) a vinylpyridine and (2) a mixture of at least one ester of an acrylic acid and a long chain aliphatic alcohol containing at least 10 carbon atoms, and at least one ester of an acrylic acid and a lower aliphatic alcohol containing not more than 6 carbon atoms, said copolymer having the vinylpyridine and the total ester mixture in a mole ratio of from 2 :1 to 1 :10 and (b) a p,p'-methylene bisphenol or the monoether derivative thereof, having attached to each aromatic ring two tertiary alkyl radicals.

The combination of the pyridine-containing copolymer (a) and the methylene bisphenol (b) imparts unexpected and superior properties to hydrocarbon oil compositions not provided by the same copolymer together with other well-known anti-oxidants such as simple phenols, *e.g.*, alkyl phenols such as 2,6-di-tertbutyl-4-methylphenol or certain other bisphenols, *e.g.*, 2,2'-methylene bis (4-methyl-6-tertbutylphenol), arylamines, *e.g.*, phenyl-alphanaphthylamine or phenyl-beta-naphthylamine.

The present combination imparts properties to hydrocarbon lubricating oils, which make them highly effective in ensuring engine cleanliness and very low wear when they are used for the lubrication of internal combustion engines, and particularly spark ignition engines which are operated on fuels which contain metal-containing substances, such as organometallic anti-knock agents. This co-action is obtained in various hydrocarbon lubricating oils, whether a mineral or a synthetic oil. Oils which are substantially paraffinic and/or naphthenic in character are preferred. They may contain substantial proportions of hydrocarbons having aromatic character but the proportions and types of components are preferably such that the viscosity index of the base oil is at least 80, preferably between 90 and 150. The viscosity may vary within wide limits so that the oils may belong, for example, to S.A.E. classes 5 W, 10 W, 20 W, 20, 30, 40 or 50.

The oil may be derived from a highly paraffinic crude, in which case distillation and/or dewaxing may be sufficient to provide a suitable base stock; a minimum of chemical or selective solvent treatment may be used if desired. Mixed base crudes and even highly aromatic crudes which contain paraffinic hydrocarbons also provide suitable oil base stocks by well known refining techniques. Usually these comprise the separation of distillate fractions of suitable boiling range followed by selective solvent extraction with solvents such as furfural or phenol to provide raffinate fractions which are suitable for further refining by dewaxing and chemical treatment such as sulphuric acid treatment. The hydrocarbon oils may be blends of different mineral oil distillates and bright stocks. Also blends of mineral oils and fatty oils, such as castor oil and lard oil and/or synthetic lubricants, such as polymerized olefins, *e.g.*, polyisobutylene may be used.

The vinylpyridines used in making the additives (a) may be exemplified by 2-vinylpyridine, 3-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine, 4-methyl-2-vinylpyridine, 5-ethyl-2-vinylpyridine and 2-butyl-5-vinylpyridine. Particularly preferred are 2-, 3- and 4-vinylpyridines and the C_{1-6} alkyl- substituted derivatives thereof.

The long chain esters used in the preparation of the additives (a) include the esters of long chain aliphatic alcohols and acrylic acid and the alpha- substituted acrylic acids such as methacrylic acid, ethacrylic acid, alpha-phenyl acrylic acid, alpha-cyclohexyl acrylic acid and chloroacrylic acid. The long-chain aliphatic alcohols may be exemplified by decyl, lauryl, cetyl, stearyl, eicosanyl and nonadecanyl alcohols and mixtures thereof. Particularly preferred esters to be used are the acrylic acid and methacrylic acid esters of aliphatic monohydric alcohols, and especially alkyl alcohols, containing from 10 to 20 carbon atoms.

Specific examples of these long chain acrylic acid esters include decyl acrylate, lauryl acrylate, stearyl acrylate, decyl methacrylate, lauryl methacrylate, cetyl methacrylate, stearyl methacrylate, eicosanyl acrylate and docosanyl acrylate and mixtures thereof.

Preferably a mixture of two or more of these long chain esters is used in making the additives (a). Preferably the alcohol parts of these esters have a difference in the number of carbon atoms of at least 4. Examples of mixtures of long chain esters are: decylmethacrylate/octadecyl methacrylate; tetradecyl methacrylate/hexadecyl methacrylate; tetradecyl acrylate/octadecyl methacrylate and dodecyl methacrylate/eicosanyl methacrylate.

Particularly superior results are obtained when one of the long chain esters is a C_{16} to C_{18} ester and the other is a C_{16} to C_{20} ester.

The different long chain esters may be employed in mol ratios from 1 :10 to 10 :1 and preferably from 1 :4 to 4 :1. The superior copolymers are obtained when the higher long

chain esters, *e.g.*, those having from 16 to 20 carbon atoms in the alcohol portion, and the lower long chain esters, *e.g.*, those having from 10 to 14 carbon atoms in the alcohol portion are combined in mol ratios from 1:1 to 1:5. Preferably the average chain length of the alcohol portions is between 12-16 carbon atoms.

In considering these mixtures, it should be noted that an ester of acrylic acid or methacrylic acid and technical lauryl alcohol, which is a mixture of straight chain alcohols, should not be considered as such a mixture since copolymers of technical lauryl methacrylate and vinylpyridine will not have a sufficient difference in the alkyl side chains. Rather technical lauryl esters function as simple esters and possess the limitations of such esters namely that the ultimate copolymers, prepared from them function as pour point depressants only in specific oils and tend to break down, form emulsion and cause corrosion. On the other hand, copolymers, prepared from said mixtures form excellent pour point depressants, detergents and viscosity index improving additives for use in lubricating oil compostions.

The lower esters, which are derived from an aliphatic alcohol of not more than 6 carbon atoms include the acrylic acid and methacrylic acid esters of methanol, ethanol, butanol, hexanol, isobutyl alcohol and propanol. Esters having 1-4 carbon atoms in the alcohol portion, such as methyl methacrylate, are preferred. Preferably these lower esters make up not more than 60 mol % such as 10-45 mol % of the total ester mixture

The fact that the copolymers containing such large proportions of the lower esters, possess the above-noted superior properties is surprising in view of the fact that polymers prepared heretofore from such lower esters failed to have many of these superior properties. The presence of the lower esters is of further advantage in that it brings about an unexpected improvement in viscosity-temperature properties.

As the vinylpyridines and the esters have different polymerization rates, the proportions in which they enter the copolymer molecule will differ from the proportions in which they occur in the reaction mixture. It will be necessary, therefore, to determine beforehand the ratio of proportions of monomers needed to give copolymers having the monomers in the required ratio. This can be easily accomplished by conducting a few routine runs and examining the composition of the resulting copolymer. The initial concentration of monomers can then be adjusted so as to give the copolymer of the desired composition.

As the reaction progresses, the monomer concentration ratios change due to the difference in the rate of polymerization, in some cases, the ratio will change so that it will not be producing copolymers having the monomers in the desired ratio. The superior products are, therefore, obtained by employing some steps during the copolymerization which will ensure that the ratio of concentrations of monomers does not vary during the reaction period from the above-described limits. This may be accomplished in a variety of ways. One way, for example, comprises stopping the copolymerization after the ratio of the monomer concentrations has reached the limiting value. This method is of particular value if the change in the ratio between the monomer concentrations during copolymerization is slow and a considerable yield of copolymer has been obtained before the limiting values have been attained.

Another method is to adjust the ratio between the monomer concentrations by adding monomer during the course of the polymerization. In this case, it is usually sufficient to add the monomer which is consumed the fastest. Such additions may be periodic or continuous.

Control over the change of ratio can be made by periodic withdrawal of samples and analyzing the product, or can be made in a homogeneous system by simply observing a physical property of the mixture which varies with the ratio of concentrations of monomers, such as boiling point, refractive index, vapour pressure, specific gravity and the like, and adding the monomer or monomers so as to bring the value up to the predetermined level for the desired product.

Preferred additives (a) have molecular weights between 50,000 and 2,500,000 as determined by the light scattering technique described in Chemical Reviews, Volume 43, page 319 (1948). Preferably, the molecular weights range from about 75,000 to 1,000,000 and more preferably from 100,000 to 660,000.

Any suitable conditions may be employed to maintain the molecular weight within the desired range. Factors which exert an influence on the molecular weight of the polymer include the method of polymerization (*e.g.*, polymerization in emulsion, suspension, solvent solution or bulk), the nature and concentration of the catalyst employed, the temperature and nature and amount of the monomers. When the polymerization is accomplished in solution, the molecular weight of the product will be lower when the dilution is greater, *i.e.*, when the concentration of solvent is greater. With the same catalyst, the higher polymerization temperature tends to give lower molecular weights.

Polymerization initiators that are particularly suited for use in preparing the claimed copolymers include various free-radical yielding catalysts as peroxide catalysts, such as, for example, benzoyl peroxide, lauroyl peroxide, tertiary butyl hydroperoxide, 2,2-bis(tertiary butyl peroxy) butane, di(tertiary butyl) peroxide, tertiary butyl perbargonate, hydrogen peroxide, sodium or potassium persulphate, percarbonate and peracetic acid. Other suitable catalysts include sodium bisulphite, diethyl sulphoxide and azo compounds, such as alpha, alpha-azodiisobutylonitrile. The amount of the initiator added may vary over a considerable range. In general, the amount of initiator added will vary from 0·1% to 5% by weight of the material being polymerized. Preferred amounts vary from 0·1% to 2% by weight.

The temperature selected is important relative to the viscosity temperature (VT) properties desired. For a given lower ester content, the higher temperatures give lower VT values. Preferred temperatures range from 40°C to 90°C. Temperatures up to 120°C or even up to 160°C may be used, but give lower VT values.

The polymerization may be conducted in the presence or absence of air. In most cases, however, it has been found desirable to conduct the polymerization in the absence of air, *e.g.*, in the presence of an inert gas such as nitrogen. Atmospheric, reduced or superatmospheric pressure may be employed.

At the end of the polymerization, any unreacted monomer or monomers and/or solvents may be removed, preferably by distillation or by precipitation with appropriate solvents.

The following examples illustrate the preparation of suitable polymers for use in oil compositions in accordance with the invention. Unless otherwise specified, parts disclosed in the examples are parts by weight.

In the examples, the molecular weights were determined by light scattering method and the ratio of vinylpyridines to ester was determined by analysis for nitrogen.

Example I

A mixture of 2·52 mol of stearyl methacrylate, 5·04 mol of lauryl methacrylate, 0·83 mol of methyl methacrylate, 1 mol of 2-methyl-5-vinylpyridine and 0·2% wt of alpha,alpha'-azodiisobutyronitrile was placed in a reaction vessel and reacted for about 24-48 hours at 65°C with stirring in a nitrogen atmosphere. The polymer was then dispersed in equal volumes of benzene and thereafter precipitated with 5-10 volumes of a mixture of acetone and methanol. This was repeated and a stearyl methacrylate/lauryl methacrylate/methyl methacrylate/2-methyl-5-vinyl-pyridine polymer having a nitrogen content of 0·60% by weight and a molecular weight in excess of 750,000 was recovered.

Following essentially the procedure of Example I, other polymers are prepared from monomer mixtures in the molar proportions as shown in Table I.

Table I

Example	SMA	LMA	MMA	BMA	MVP	EVP
II	2.24	4.48	1.86		1	
III	2.24	4.48		1.86	1	
IV	2.05	3.92	2.43		1	
V	2.05	3.92		2.43	1	
VI	1·68	3.36	3.36		1	
VII	1.68	3.36		3.36	1	
VIII	1.40	2.80	4.2		1	
IX	1.40	2.80		4.2	1	
X	1.12	2.24	5.04		1	
XI	1.12	2.24		5.04	1	
XII	2.52	5.04	0.83			1
XIII	2.24	4.48		1.86		1
XIV	2.05	3.92	2.48			1
XV	2.05	3.92		2.43		1

SMA = Stearyl methacrylate
LMA = Lauryl methacrylate
MMA = Methyl methacrylate
BMA = Butyl methacrylate
MVP = 2-Methyl-5-vinylpyridine
EVP = 5-Ethyl-2-vinylpyridine

Other examples of useful polymers for the purpose of the invention include: dodecyl acrylate/stearyl acrylate/ethyl methacrylate/vinylpyridine; hexadecyl methacrylate/stearyl methacrylate/propyl methacrylate/2-methyl-5-vinylpyridine; lauryl methacrylate/stearyl methacrylate/ethyl methacrylate, 5-ethyl-2-vinylpyridine and decyl methacrylate/octadecyl methacrylate/butyl methacrylate/vinylpyridine.

Example XVI

29·3% Stearyl methacrylate, 49·7% lauryl methacrylate, 16% methyl methacrylate and 5·0% methyl vinylpyridine were charged to a 1140 liter stainless steel autoclave. A 50/50 mixture of benzene and neutral petroleum oil was added to the autoclave so as to furnish 1 part of the mixture per 3 parts of the total monomer. 0·25% of di-tertbutyl peroxide was then added and the mixture heated at 120°C for about seven hours.

At the completion of the reaction, the benzene was stripped off of final conditions of 120°C and 10 mm Hg. The benzene-free product was then diluted with neutral oil to a polymer content of about 30% by weight and filtered at 100-120°C.

Example XVII

Example XVI was repeated with the exception that the proportion of methyl methacrylate in the feed mixture was varied from 16% to 30%. The resulting copolymers were then added to the base oil as in the preceding example.

Example XVIII

Example XVII was repeated with exception that the catalyst was as in Example I and the temperature was 55°C. The resulting copolymers were then addded to the base oil as in the preceding example.

Example XIX

Example XVI is repeated with the exception that the methyl methacrylate is replaced by hexyl acrylate.

Example XX

Example XVI was repeated with the exception that the methyl methacrylate was used in an amount of 14% and the lauryl methacrylate and stearyl methacrylate were present in the mol ratios of 1·8 to 1, respectively, amounting to 81% of the total polymer mixture and the end product had a molecular weight of 5×10^5 and a nitrogen content of 0·60%

The additives (b) preferably contain C_{4-12} and still better C_4 tertiary alkyl groups, preferably in the 2,6-position. The monoether derivative may contain a C_{1-10} preferably C_{1-6} alkyl, aryl or cycloalkyl radical in the ether group.

The additives (b) may be prepared by any suitable means such as by reacting a di-tertiary alkyl phenol with formaldehyde in the presence of an organic solvent such as heptane and an acidic catalyst such as sulphuric acid. Another method is to react the di-tertiary alkyl phenol with formaldehyde in the presence of an acid catalyst in an aqueous medium. The ether of the bisphenol can also be prepared by suitable means such as by reacting a methylene bisphenol, e.g., methylene bis(di-tertalkyl phenol) with a methyl halide such as methyl chloride in the presence of base compounds like KOH in methyl alcohol. The general method of preparing these compounds is well known in the art and does not form a part of the present invention. Compounds of this type include 4,4'-methylene bis(2,6-ditert-butyl phenol), 4,4'-methylene bis(2,3-di-tert-butyl phenol), 4,4'-methylene bis(2,5-di-tert-butyl phenol), 4,4'-methylene bis(3,5-di-tert-butyl phenol), 4,4'-methylene bis(2,6-ditert-octyl phenol), 4,4'-methylene bis(2-tert-butyl, 6-tert-octyl phenol), 4,4'-methylene bis(1-tert-butyoxy 2,6-ditert-butyl phenyl 2,6-di-tert-butyl phenol), and mixtures thereof.

Minor amounts of each class of additives are sufficient for a highly effective combination. Additive (a) may be used in a proportion of 0·1-10%, preferably 0·2-5% by weight, based on the whole composition, and additive (b) may be used in a proportion of 0·05-2% preferably 0·1-1% by weight based on the whole composition.

The foregoing combination of additives (a) and (b) appears to co-act with certain phosphorus compounds to give unexpected improvement in anti-wear and anti-scuffing. These phosphorus compounds may be used in proportions of 0·01-2%, preferably 0·1-1% by weight, based on the whole composition and are partial or full esters of an organic phosphorus compound. Phosphorus compounds of this type include alkyl, cycloalkyl, alkaryl, aralkyl and aryl phosphites, phosphates, phosphonates, and their thio-derivatives, such as C_{3-81} alkyl phosphites, e.g., di and tributyl, octyl, lauryl, stearyl, cyclohexyl, benzyl, cresyl, phenyl phosphites or phosphates, as well as their thio-derivatives; P_2S_5-terpene reaction product, P_2S_5-pine oil reaction product and metal salts thereof such as Na, K, Ca or Ba salts of P_2S_5-terpene reaction product; dibutyl methane-phosphonate, dibutyl trichloromethane-phosphonate, dibutyl monochloromethanephosphonate, dibutyl chlorobenzene phosphonate, dibutyl monochloromethanephosphonate and dibutyl chlorobenzenephosphonate. The esters of pentavalent phosphorus acids such as diphenyl, dicresyl, triphenyl, tricresyl, trilauryl and tristearyl ortho phosphates, P_2S_5-terpene reaction products and mixtures thereof are preferred.

The following non-ash forming compositions are representative of the invention, the percentages being by weight.

Composition A

Example XX copolymer	5%
4,4'-methylene bis(2,6-ditert-butyl phenol)	0·5%
Tricresyl phosphate	0·8%
Mineral lubricating oil (10W-30)	Balance

Composition B

Example XX copolymer	5%
4,4'-methylene bis(2,6-di-tert-butyl phenol)	0·5%
Tricresyl phosphate	0·8%
Dicresyl phosphate	0·08%
Mineral lubricating oil (10W-30)	Balance

Composition C

Example XX copolymer	5%
4,4'-methylene bis(2,6-di-tert-butyl phenol)	0·5%
Cycloalkyl-thiophosphate	1·28%
Mineral lubricating oil (10W-30)	Balance

Composition D

Example XIX copolymer	5·5%
4,4'-methylene bis(2,6-di-tert-butyl phenol)	0·5%
Glycerol monooleate	0·5%
P_2S_5-Olefin reaction product	0·5%
Stearic acid	0·1%
Mineral lubricating oil (blend of 100 and 250 HVI neutral containing about 6% bright stock)	Balance

Properties: Specific gravity 1·165, flash point 250°F, pour point 50°F, SUS viscosity at 210°F 150

Composition E

Example I copolymer	3%
4,4'-methylene bis(2,6-di-tert-butyl phenol)	0·3%
Diphenyl phosphate	0·5%
Mineral lubricating oil (solvent refined, VI 95, SAE 30)	Balance

Composition F

Example II copolymer	2·5%
4,4'-methylene bis(2,6-di-tert-butyl phenol)	0·3%
Mineral lubricating oil (Aviation Grade)	Balance

Other representative non-ash forming lubricating compositions of this invention include mineral oils containing: G, 1·5% copolymer of Example X + 0·2% 4,4'-methylene bis-(3,5-di-tert-butylphenol); H, 2% copolymer of Example XX + 0·5% 4,4'-methylene bis (2,6-di-tert-octylphenol); 2·5% Example V copolymer + 0·3% 4,4'-methylene bis(2,6-di-tert-octylphenol); J, 2·5% Example III copolymer + 0·3% 4,4'-methylene bis(2,6-di-tert-butylphenol) + 0·1% tricresyl phosphate; K, 3% Example I copolymer + 0·25% 4,4'-methylene bis(2,6-tert-butyl-6-methoxy phenol); and L, 3% Example II copolymer + 0·25% 4,4'-methylene bis(2-tert-butyl-6-tert-octyl-phenol).

The present lubricating compositions were tested in (I) the Chevrolet Sludging Test modified EX-3 (V-8) described in

CRC Progress Report No. 3, June 1, 1957; (II) the Chevrolet L-4 Test described in the CRC Handbook; (III) 100 Hours Cadillac LS-3 Test Cycle conditions as noted repeated to total 100 hours: 1 minute idle, 500 rpm, 75°F jacket temperature; 18 minutes, 2500 rpm, 37 BHP (brake horse power), 170-180°F jacket temperature; 4 minutes, 3200 rpm, 57 BHP, 200°F jacket temperature; (IV) the 400 hours Cadillac LS-4 Test Cycle condition repeated to total 400 hours: 4 minutes idle, 500 rpm, 75°F jacket temperature; 7 minutes idle, 950 rpm, 10 BHP, 130°F jacket temperature; 5 minutes idle 1900 rpm, 33 BHP, 190°F jacket temperature; 7 minutes idle, 160 rpm, 33 BHP, 130°F jacket temperature; 5 minutes idle, 2850 rpm, 95 BHP, 190°F jacket temperature; (V) the General Motor's MS Test described in AMA (Automotive Manufacturers Association).

Proposed Test Procedure Minutes for Motor Oils for ASTM Test Procedure, Boston Meeting August 1958: (VI) the 5000 mile Field Test; and (VII) the Petter Single Cylinder Gasoline Engine Test LA 3/A, Operating procedure: time, 48 hours; speed, 1540 rpm; induction air temperature, 50°C. jacket coolant temperature, 160°C, sump oil temperature, 130°C;

TABLE II

(I) *Chevrolet Modified EX-3 (V 8) Sludging Test*

Composition	Varnish[1] Piston	Varnish[1] Total	Sludge[1] Total	Final[2] Rating
B	8.9	8.5	9.3	88.6

(II) *Chevrolet L-4 Test*

Composition	Varnish[1] Piston	Final[2] Rating	Cu-Pb Bearing weight loss mg.
A	9.4	94.7	210
B	7.3	84.3	122

Note: In I and II (1) 10=perfect, (2) 100=perfect.

(III) *100 Hours Cadillac Test*

Composition	Lacquer	Sludge	Intake Valve	Overall Cleanliness	Oil ring plugging %	Burned exhaust Valves	Average top ring wear(mg)
B	98.0	96.4	73.0	97.2	0	0	29.2

(IV) *400 Hours Cadillac LS-4 Test*

Composition	Lacquer[2]	Sludge[2]	Grey Paint[2]	% Oil ring filling[2]	Rust[2]	Maximum cylinder wear(mm)	Burned exhaust valves
A	45	46	48	7	48	0.0035	None

Note: (1) 10=perfect, (2) 50=perfect.

(V) *General Motors MS Test*

Composition	Total Sludge[1]	Total Varnish[1]	Rust[1]
C	9.5	9.5	8.6
GM Specification: (4745M)	8 minimum	8.5 minimum	8 minimum

(VI) *Field Test Visual Rust Rating*

Composition	Lifters[1]	Push rod[1]	Rocker Arm Covers[1] Rust rating	Rocker Arm Covers[1] CRC lacquer rating
A	10	10	10	8.7

Note: (1) 10=perfect.

(VII) *Petter LA 3/A Engine Cleanliness Test*

Composition	Skirt[1]	Under-crown[1]	Oil Ring[1]	Ring Sticking
1. Mineral oil[a])	1	1	5½	100° at 16 hours
2. Mineral oil[a])+1%4,4¹¹-methylene bis(2,6-ditert-butyl,henol)	5½	4	6	No e
3. Mineral oil[a])+1% c clo-alkyl thiophosphate	2½	1	6	130° at 48 hours
4. Mineral oil[a])+4% copolymer of Ex XX	7	6½	5½	3[illegible]° at 48 hours
5. (4)+1% 2,6-di-t-butyl-alpha-dimethylamino-p-cresol	6	4½	7	360° at 48 hours
6. (2)+4% copolymer of Ex XX	8½	5½	7	None
7. (3)+4% copolymer of Ex XX	7	7	6½	None

Note: (1) 10=perfect; (a) blend of mineral oil having flash point 400-490°F, Viscosity Red I at 140°F of 100, Pour Point 10-15°F, said blend containing about 15% Bright Stock.

Lubricating oil compositions of this invention are particularly applicable for high temperature high speed use as in aviation engines, automotive engines and truck engines, as well as industrial equipment operating under the conditions described in this invention.

We claim:

1. A hydrocarbon lubricating oil composition comprising a major proportion of a hydrocarbon lubricating oil and minor proportions of (a) an oil-soluble copolymer of (1) a vinylpyridine and (2) a mixture of at least one ester of an acrylic acid and a long chain aliphatic alcohol containing at least 10 carbon atoms, and at least one ester of an acrylic acid and a lower aliphatic alcohol containing not more than 6 carbon atoms, said copolymer having the vinylpyridine and the total ester mixture in a mole ratio of from 2:1 to 1:10, and (b) a p,p'methylene bisphenol or the monoether derivative thereof, having attached to each aromatic ring two tertiary alkyl radicals.

2. A composition as claimed in Claim 1, wherein additive (a) has an average molecular weight between 5×10^4 and $2{\cdot}5\times10^5$.

3. A composition as claimed in Claim 1 or 2, wherein the lower ester makes up not more than 60 mol % of the total ester mixture.

4. A composition as claimed in any one of claims 1-3, wherein the lower ester makes up 10-45 mol % of the total ester mixture.

5. A composition as claimed in any one of Claims 1-4, wherein the lower ester is derived from a C_{1-4} alcohol.

6. A composition as claimed in any one of Claims 1-5, wherein the lower ester is methyl methacrylate.

7. A composition as claimed in any one of Claims 1-6, wherein a mixture of at least two of the long chain esters is employed.

8. A composition as claimed in Claim 7, wherein the alcohol parts of said esters have a difference in the number of carbon atoms of at least 4 and the average chain length of the alcohol parts is between 12-16 carbon atoms.

9. A composition as claimed in Claim 7 or 8, wherein the different long chain esters are present in mol ratios from 1:10 to 10:1.

10. A composition as claimed in any one of Claims 7-9, wherein the different long chain esters are present in mol ratios from 1 :4 to 4 :1.

11. A composition as claimed in any one of Claims 7-10, wherein the mol ratio of the higher long chain ester to the lower long chain ester is 1 :1 to 1 :3.

12. A composition as claimed in any one of Claims 7-11, wherein a mixture of a C_{10-14} ester and a C_{16-20} ester is employed.

13. A composition as claimed in any one of Claims 7-12, wherein a mixture of lauryl and stearyl methacrylate is employed.

14. A composition as claimed in any one of Claims 1-13, wherein the vinylpyridine is a 2-, 3- or 4- vinylpyridine.

15. A composition as claimed in any one of Claims 1-14, wherein the vinylpyridine is 2-methyl-5-vinylpyridine.

16. A composition as claimed in any one of Claims 1-15, wherein additive (a) is present in a proportion of 0·1-10% by weight, based on the whole composition.

17. A composition as claimed in any one of Calims 1-16, wherein additive (a) is present in a proportion of 0·2-5% by weight, based on the whole composition.

18. A composition as claimed in any one of Claims 1-17, wherein additive (b) has attached to each aromatic ring two C_{4-12} tertiary alkyl radicals.

19. A composition as claimed in any one of Claims 1-18, wherein additive (b) has attached to each aromatic ring two C_{4-8} tertiary alkyl radicals.

20. A composition as claimed in any one of Calims 1-19, wherein the tertiary alkyl radicals of additive (b) are present in the 2,6-position.

21. A composition as claimed in any one of Claims 1-20, wherein additive (b) is a monoether derivative containing in the ether group a C_{1-10} alkyl, arvl or cycloalkyl radical.

22. A composition as claimed in any one of Claims 1-21, wherein additive (b) is a monoether derivative containing in the ether group a C_{1-8} alkyl, aryl or cycloalkyl radical.

23. A composition as claimed in any one of Claims 1-20, wherein additive (b) is 4,4'-methylene bis (2,6-di-tert-butylphenol).

24. A composition as claimed in any one of Claims 1-23, wherein additive (b) is present in a proportion of 0·05-2% by weight, based on the whole composition.

25. A composition as claimed in any one of Claims 1-24, wherein additive (b) is present in a proportion of 0·1-1% by weight, based on the whole composition.

26. A composition as claimed in any one of Claims 1-25, additionally containing a minor proportion of an organic phosphate.

27. A composition as claimed in Claim 26, wherein the organic phosphate is an aryl phosphate.

28. A composition as claimed in Claim 26 or 27, wherein the organic phosphate is tricresylphosphate.

29. A composition as claimed in Claim 26, wherein the organic phosphate is a cycloalkyl thiophosphate.

30. A composition as claimed in any one of Claims 26-29, wherein the organic phosphate is present in a proportion of 0·01-2% by weight, based on the whole composition.

31. A composition as claimed in any one of Claims 26-30, wherein the organic phosphate is present in a proportion of 0·1-1% by weight, based on the whole composition.

32. A composition as claimed in any one of Claims 1-31, wherein the hydrocarbon lubricating oil is a mineral lubricating oil.

33. Lubricating oil compositions, substantially as hereinbefore described.

R. HALL

of REMFRY & SON

Agent for the Applicants.

Dated this 29th day of December 1960.

MGIP Sanl'h—SL—38 Patent/62—25-3-63—100.

For INSPECT

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74729, 29th December 1960, 8th Paus 1882 (Saka).
(Accepted 26th May 1962.)

ORGANIC COMPOSITIONS HAVING IMPROVED OXIDATION STABILITY.

SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N V., a Netherlands Research Company, at 30, Carel van Bylandtlaan, The Hague, The Netherlands.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to organic compositions, having improved oxidation stability.

Many organic materials such as fuels, lubricating oils, greases, waxes, asphalts and synthetic resins have been developed for various purposes. It is customary to incorporate in such products one or more of various phenolic or aromatic amine oxidation inhibitors Compounded compositions of this type, although effective under moderate temperature and pressure conditions, are relatively ineffective at high temperatures and pressures, resulting in the breakdown and formation of sludge and solid deposits which are undesirable because they cause wear and damage. Recently, attempts have been made to overcome this defect and to improve not only the oxidation stability of organic materials but other properties as well, by combining well known antioxidants (phenols and amines) with certain non-ash forming polymeric compounds. However, any enhanced benefit in the use of such combinations for oxidation stability is of short duration

It has now been discovered that the oxidative stability of organic materials, such as for example petroleum products, containing polyhydric phenolic compounds (a) is considerably improved and the general behaviour of such compounded materials considerably improved by the addition thereto of aryl acid phosphate (b).

The additives (a) preferably have the formula A of the accompanying drawings, wherein Ar is an aromatic group, R is a C_{1-8} alkyl group, X is oxygen, sulphur or a branched or straight chain alkylidene group having from 1-5 carbon atoms, Y is hydrogen, -OH or group of the formula C of the drawings, n is an integer of at least 1, preferably 2, and m and q are each an integer of 0 or 1; at least one of them being 1. Preferred additives (a) have the formula A, of the drawings, wherein R is as defined in formula (A) of the drawings X is a branched or straight-chain alkylidene group having from 1-5 carbon atoms, and Y is - OH or group of the formula X of the drawings. Still more preferred additives (a) have the formulae A_2 and A_3 of the drawings, wherein the R's are tert-alkyl groups. Preferred are the phenols of the formulae (A_2) and (A_3) of the drawings wherein the R's are tertiary alkyl groups being in ortho position with respect to the phenolic hydroxyl group. Such phenols have the formula Y of the drawings, wherein the R's are tertiary alkyl radicals.

The A-type phenols include 3,3', 5,5'-tetraisopropyl-4,4'-dihydroxydiphenyl, 3,3'-dimethyl-5,5 -ditert . amyl-4,4'-dihydroxydiphenyl; 1,1-bis(3,5-ditertbutyl - 4-hydroxyphenyl)methane; 1,1-bis(3,5 diisopropyl - 4-hydroxyphenyl)methane; 1,1-bis(3,5-di-sec - butyl - 4 - hydroxyphenyl)methane; 1,1-bis(3 - isopropyl - 5-tert-butyl 4-hydroxyphenyl)methane; 1,1-bis(3,5-di(2-octyl)-4-hydroxyphenyl)methane; 1,1-bis(3-sec-butyl - 5(2-hexyl)4-hydroxyphenyl)methane; 1,1-bis(3' - isopropyl-5 - (1,1,3,3-tetramethyl-butyl)4 - hydroxyphenyl)methane; 1,1-bis(3-tert-butyl-5 . methyl - 2-hydroxyphenyl)methane; 1,1-bis(3-tert-butyl 5-methyl-2-hydroxyphenyl)ethane; 1,1-bis(3-tert-butyl . 5-methyl 2-hydroxyphenyl)propane; 1,1-bis(3-tert-butyl-5 - methyl-2-hydroxyphenyl)isobutane; 1,1-bis(3-methyl-5-tert-butyl . 6-hydroxyphenyl)methane; 1,1-bis-(3,5-ditert-butyl-4-methoxyphenyl; 3,5-di - tert-butyl-4-methylphenyl)methane; 1,1-bis(3,5-di-tert . butyl-4-hydroxyphenyl)ether; 4,4-thio - bis(6-tert - butyl-o-cresol). The A-type phenols include 2,6-di-tert-butyl, 2,6-dimethyl, 2-tert-butyl, 6-methyl-, 2,2-ditert-butyl, 2,6-dicyclohexyl-, 2-methyl-6-propyl-, 2-methyl-6-hoxyl 4 methylol phenols.

The additives (b) preferably have the formula B of the drawings wherein the X's are independently selected from oxygen and sulphur, preferably all being oxygen, R_1 is hydrogen or a hydrocarbon group, preferably an aryl group and R_2 is an aryl group, preferably a C_{1-18} alkyl substituted aryl group, such as a C_{1-9}alkyl substituted phenyl group.

Preferred additives (b) have the formulae B_1 and B_2 of the drawings or are mixtures of B_1 and B_2 of the drawings.

The compounds of this class may be specifically illustrated by phenyl, naphthyl, C_{1-18} alkylphenyl, *e.g.*, methyl, ethyl, butyl, dimethyl, diisopropylphenyl monoacid and diacid phosphates and thiophosphates of which preferred are monocresyl and dicresyl acid phosphates and mixtures (*e.g.*, in a weight ratio 1:1) thereof.

Under certain conditions the addition of a third additive (c) having the formula Z of the drawings, wherein X and each R_2 are the same as in additive (b), is desirable, particularly when the organic material such as a mineral oil lubricant is subjected to extreme temperatures pressure, and corrosive conditions. Such phosphates (c) include triphenylphosphate, tricresylphosphate, tricresylthiophosphate and tributylphenylphosphate. Each of the additives (a), (b) and (c) may be used in proportions of 0.001-5, preferably 0.01-2.5 per cent. by weight, based on the whole composition

The additive combinations of this invention effectively stabilise various organic materials such as oleaginous materials, polymers, fuels, waxes, resins and particularly inhibits oxidation and reduces corrosivity of liquid hydrocarbons such as gasoline, jet fuels, transformer oils, turbine oils, mineral lubricating oils, and industrial oils such as cutting fluids and quenching fluids. The anti-oxidant and stabilizing additive combination is particularly useful in highly refined mineral oils of the lubricating oil viscosity range (SAE 10W, SAE 20) from which natural occurring oxidation inhibitors have been removed by refining. Furthermore, synthetic hydrocarbon oils and resins such as olefin polymers, *e.g.*, ethylene propylene, isobutylene/octadecene and isobutylene/styrene copolymers, as well as synthetic oils of the ester type, *e.g.*, di-2-ethyl-hexylsebacate, are improved by the additive combination of this invention.

The unexpected results obtained by use of the additive combination of the invention are demonstrated by results of evaluations of the additives in a refined mineral white oil, using (I) the Dornte Oxidation Stability Test described in National Petroleum News, September 17, 1941, pages R-294-296, using iron catalyst at 150°F. and (II) the Copper Strip Corrosion Test at 300°F., wherein the rating was 0 to 10 with 10 being poor and zero being excellent. The properties of the white oil are Gr °API 29-31; Color, 30 min.; Pour point °F . Max. 15; Flash point COC °F., Min. 420, Viscosity, SUS at 100°F, 345-355; Unsaponifiable Residue, Min. 98. The results are shown in Table I.

TABLE I.

Additive	(I) Oxidation Test Induction Period (hours)	(II) Cu Strip Rating
(1) None	0·3	10
(2) 0·04% dicresylphosphate	4	8
(3) 0·25% 1, 1'-bis (3, 5-di-tert-butyl-4-hydroxy phenyl)-methane	43	
(4) (3)+ 0·4% tricresylphosphate	43	8
(5) (2)+(4)	76·5	0
(6) (2)+(3)	91·5	3
(7) 0·02% dicresylphosphate + 0·02% monocresyl phosphate + (3)	21·5	3

From the results presented in Table I it can be seen that compositions of the present invention (5, 6 and 7) are from 2 to 18 times as effective in inhibiting oxidation than are compositions (2, 3, and 4) which contain only one of the additives. Compositions 5, 6 and 7 of the present invention are superior in corrosion inhibition to other compositions such as 1-4.

Other compositions of this invention which would give results comparable to Compositions 5, 6 and 7 include:

(8) SAE 30 mineral oil + 0.2 per cent. 1,1-bis(3,5-di-tert-butyl-4-hydroxyphenyl) methane + 0.02 per cent. monocresyl-phosphate + 0.02 per cent. dicresylphosphate.

(9) White oil + 0.2 per cent. 2,6-di-tert-butyl 4-methylolphenol + 0.04 per cent. dicresylphosphate.

(10) SAE 30 mineral oil + 0.3 per cent. 2,6-di-tert.-butyl-4-methylolphenol + 0.06 per cent. dicresylphosphate + 0.1 per cent. tricresyl-phosphate.

(11) SAE 30 mineral oil + 0.6 per cent. 1,1-bis(3,5-di-tert.-butyl-4 -hydroxyphenyl) methane + 0.08 per cent. dicresylphosphate + 0.1 per cent. tricresylthiophosphate.

Compositions of this invention are useful for providing stability and other desired properties to petroleum products such as mineral lubricating oils which also contain small amounts (0.1 per cent. to 3 per cent.) of other agents such as metal detergents such as metal organic sulphonates, *e.g.*, neutral or basic Ca, Ba, or Zn petroleum sulphonates; anti-wear agents such as metal thiocarbamates, *e.g.*, Zn, Cr, or Ca dibutyl or diamyl dithiocarbamate, viscosity-index improvers, pour point depressants and non-ash forming detergents such as the oil-soluble polymethacrylates available under the name "Acryloids" and specifically, "Acryloid" 150, 618, 710, 768, described in U. S. patent 2,710,842 or "Acryloids" of the 900 series, *e.g.*, 917 and 960 described in British patent 808,664 which are vinyl pyrrolidone alkyl methacrylate copolymers or other nitrogen containing copolymers such as dodecyl methacrylate/diethylaminoethyl methacrylate copolymer or vinyl pyridine/alkyl methacrylate copolymers described in British Patent 807,73 and U. S. Patents 2,737,496 and 2,889,282; extreme pressure agents such as aliphatic amine salts of mono- or trichloromethanephosphonic acid, or the ester or amide of such acids: alkyl thiamethyl-phosphonic acid or esters thereof such as mono or dibutyl decyl mercaptomethyl phosphonate, organic sulphides, *e.g.*, dibenzyl disulphide and mixtures thereof.

We claim:

1. An organic composition having improved oxidation stability, comprising petroleum products and
(a) a polyhydric phenolic compound and
(b) an aryl acid phosphate.

2. A composition as claimed in Claim 1, wherein the petroleum product is an oleaginous product.

3. A composition as claimed in Claim 1 or 2, wherein the petroleum product is a hydrocarbon oil.

4. A composition as claimed in any one of Claims 1-3, wherein the additives (a) and (b) each are present in a proportion of 0.001-5 per cent. by weight, based on the whole composition.

5. A composition as claimed in any one of Claims 1-4, wherein the additives (a) and (b) each are present in a proportion of 0.01-2.5 per cent. by weight, based on the whole composition.

6. A composition as claimed in any one of Claims 1-5, wherein additive (a) has the formula A of the accompanying drawings, wherein Ar is an aromatic group, R is a C_{1-8}alkyl group, X is oxygen, sulphur or a branched or straight-chain alkylidene group having from 1-5 carbon atoms, Y is hydrogen, -OH or group of the formula C of the drawings, n is an integer of at least 1, and m and q are each an integer of 0 or 1, at least one of them being 1.

7. A composition as claimed in Claim 6, wherein n is 2.

8. A composition as claimed in Claim 6 or 7, wherein X is a branched or straight-chain alkylidene group having from 1-5 carbon atoms

9. A composition as claimed in any one of Claims 6-8, wherein Y is -OH.

10. A composition as claimed in any one of Claims 6-8, wherein Y is group of the formula X of the drawings and R is a C_{1-8} alkyl group.

11. A composition as claimed in any one of Claims 6-10, wherein R is a tertiary alkyl group.

12. A composition as claimed in any one of Claims 6-11, wherein R is a tertiary butyl group.

13. A composition as claimed in any one of Claims 6-12, wherein R is in ortho position with respect to -OH.

14. A composition as claimed in any one of Claims 1-8 and 10-13, wherein additive (a) is 1,1-bis(3,5-di-tert-butyl-4-hydroxyphenyl methane.

15. A composition as claimed in any one of Claims 1-8 and 11-13, wherein additive (a) is 2,6-di-tert-butyl-4-methylolphenol.

16. A composition as claimed in any one of Claims 1-15, wherein additive (b) has the formula B of the drawings, wherein each X is oxygen or sulphur, R_1 is hydrogen or a hydrocarbon group and R_2 is an aryl group.

17. A composition as claimed in Claim 16, wherein each X is oxygen.

18. A composition as claimed in Claim 16 or 17, wherein R_1 is an aryl group

19. A composition as claimed in any one of Claims 16-18, wherein R_1 and/or R_2 is a C_{1-18} alkyl substituted aryl group.

20. A composition as claimed in any one of Claims 16-19, wherein R_1 and/or R_2 is a C_{1-5}alkyl substituted phenyl group.

21. A composition as claimed in any one of Claims 16-20, wherein additive (b) is dicresylphosphate.

22. A composition as claimed in any one of Claims 16, 17, 19 and 20, wherein additive (b) is monocresylphosphate.

23. A composition as claimed in Claims 21 and 22, wherein additive (b) is a mixture of mono- and dicresyl-phosphate

24. A composition as claimed in any one of Claims 1-23, additionally containing an additive (c) having the formula Z of the drawings wherein X_1 and each R_3 are the same as in additive (b).

25. A composition as claimed in Claim 24, wherein additive (c) is tricresylphosphate.

26. A composition as claimed in any of Claims 1 to 25, substantially as hereinbefore described

R. HALL
and
REMFRY & SON,
Agent for the Applicants.

Dated this 29th day of December 1960.

M(IPC)—L—104 Patent/ 2—20.4.63—100

SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V.

No. 74729 of 1960.

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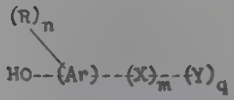
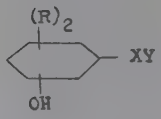
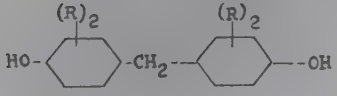
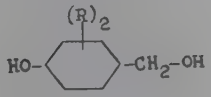
A 

A1 

A2 

A3 

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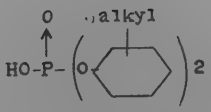
B1 

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Agent for the Applicants

REG. NO. 2273 E/44 -106'63.

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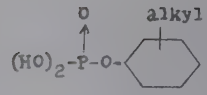

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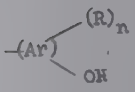

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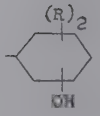

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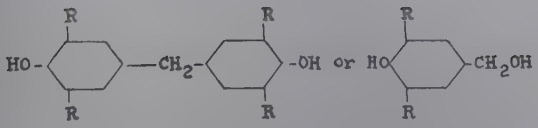

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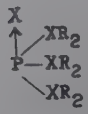

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REG. NO. 2273 E/44—106'63.
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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74730, 29th December 1960. 8th Paus 1882 (Saka) (Patent of Addition to No. 73969.) (Accepted 29th June 1962.)

PROCESS FOR THE PRODUCTION OF METAL CONTAINING REACTIVE DYESTUFFS SUITABLEFOR LYEING OR PRINTING TEXTILE MATERIAL AND CELLULOSE FIBRES AND PRODUCTS DYED OR PRINTED THEREWITH.

J. R. GEIGY A.-G., A BODY CORPORATE ORGANISED ACCORDING TO THE LAWS OF SWITZERLAND, OF 215, SCHWARZ WALDALLEE, BASLE, SWITZERLAND.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

The present invention constitutes an improvement in or modification of the invention described and claimed in the Indian patent specification No. 73969.

The invention concerns metal-containing dyestuffs which can be fixed onto cellulose fibres, processes for the production thereof, their use for the attainment of fast dyeings and the material fast dyed with the aid of these dyestuffs.

In the Indian patent application No. 73969, metal-containing dyestuffs are described in which a metal of the atomic numbers 24-29 is co-ordinated tricyclically at a formazane compounds. The metal-free formazane compounds which are the basis of these heavy metal-containing dyestuffs contain a metalisable group in o-position to the formazane chain at each of the two external aromatic radicals.

On further work being done on the subject of the invention, it has now been found that more valuable heavy metal-containing dyestuffs are obtained with such formazane compounds, which compounds contain only one metallisable group in o-position to the azo group at one of the externally azo-linked aromatic radicals. These new dyestuffs in which the heavy metal is dicyclically co-ordinated to a formazane compound, correspond to the general formula I of the accompanying drawings,

In this formula:

R represents a monovalent substituent, in particular an electrophilic radical, for example, a monovalent aromatic-isocyclic or aromatic-heterocyclic or araliphatic radical, a nitro-, cyano-, carbacyl- or aryl- carbonylamino group,

A & B each represent the radical of an aromatic-isocyclic or aromatic-heterocyclic diazo component, in particular a radical of the benzene or naphthalene series,

X represents a metal binding group in o-position to the azo bond, preferably an oxy, carboxy or sulphonylamido group,

Y represents a strongly acid dissociating, salt-forming, water solubilising group, preferably the sulphonic acid group but also the carboxyl group, phosphonic acid or an acylated sulphamide group whereby different Y's in the dyestuff molecule can also have different meanings within the definition given above.

Z represents a 2,4-dihalogen-1,3,5-triazinyl radical, a 2-alkoxy-, 2-alkyl-, 2-aryl-, 2-amino-, 2-alkylamino-, 2-arylamino-, 2-ureido-, 2-guanidino-4-halogen-1,3,5-triazinyl-(6)-radical, a 2,4- or 4,6-dihalogenpyrimidyl radical possibly substituted in 5-position by a halogen atom, a nitro, acyl, cyano, alkyl, or aryl group, a 2,6-dihalogenpyrimidyl-4-carbonyl group, a β-halogenalkanoyl, a β-halogenalkenoyl or a β-halogenalkyl-sulphamylbenzoyl radical, bound to A or B by way of a primary or secondary amino group or aminobenzoylenamino group.

By the term "halogen", as used throughout the specification, is meant chlorine or bromine.

Me represents a heavy metal of the atomic numbers 24-29, preferably copper, or then nickel, cobalt or chromium;

n represents a positive whole number of 1 to 5, and m represents a positive whole number of at most 2.

In particularly valuable and, therefore, preferred dyestuffs according to the invention, Me represents copper and A and B represent radicals of diazo components of the benzene or also the naphthalene series, and R is an organic substituent, in particular a radical of the benzene or also the naphthalene series.

The dyestuffs according to the invention are obtained by various processes. The first consists in reacting metal-containing dyestuffs of the general formula 1 wherein A and B, are radicals of diazo components, with an acylatable primary or secondary amino group or acylatable aminobenzoylenamino group and R, X, Y, Me, m and n have the meanings given above, with suitable acylating agents as given hereinbelow introducing the substituent Z, the reaction being performed under the condition given hereinbelow, so that, on completion thereof, the dyestuff still contains a substituent which easily reacts with alkalies while splitting off an anion, advantageously a mobile halogen atom of the atomic numbers 17 and 35. Principally cyclic carbimide halides which contain several reactive groups of formula IV, wherein Hal represents halogen of the atomic numbers 17 and 35, are suitable acylating agents. These are particularly halogen azine compounds of aromatic character which contain at least 2 tertiary ring N atoms and at least two mobile halogen atoms of the atomic numbers 17 and 35 at ring C atoms vicinal to such N atoms, *i.e.* for example, 2, 4, 6-trichloro-1,3,5-triazine or 2,4,6-tribromo-1,3,5-triazine, 2-alkoxy- or 2-alkyl- or 2-phenyl- or 2-amino- or 2-alkylamino- or 2-phenylamino- or 2-sulphophenylamino- or 2-ureido- or 2-guanidino- 4,6-dichloro-1,3,5-triazines or -4,6-dibromo-1,3,5-triazines, 2,4- or 4,6- dichloro- or 2,4- or 4,6-dibromo-pyrimidines which in the remaining positions contain other substituents in particular other halogen atoms or negative groups such as nitro, acyl, cyano or also only alkyl or phenyl groups; in addition a 2,6-dihalogenpyrimidyl-4-carboxylic acid halide. Also β-halogen alkanoyl halides or anhydrides, in particular β-halogen alkenoyl halides or anhydrides can be used with halogens of the atomic numbers 17 and 35, of these in particular β-chloro- or β-bromo- crotonic acid chloride or bromide, also m-(β-chlorоethylsulphamyl)-benzoyl chloride or m-(β-bromoethylsulphamyl)-benzoyl chloride. The reaction conditions are so chosen that two previous exchange of mobile groups does not occur either due to too high pH value of the reaction medium or to too high temperature. Thus the reaction is performed advantageously with the aqueous solutions of the alkali metal salts of the metal-containing dyestuffs at temperatures and pH values as low as possible, if necessary in the presence of mineral acid buffering agents such as alkali metal salts of low fatty acids, *i.e.* at pH values of about 2-7 and at temperatures of 0 to about 60°C, depending on the stability of the acylating agent or on the mobility of the substituents in the group Z which can be exchanged. The acylating agents are used in at least the equimolecular amount or, in the presence of several acylatable amino groups, in an amount which is a multiple of such groups, and they are used in fine dispersion, for example, as suspensions or emulsions, such suspension of emulsion being obtained possibly with the aid of inert organic solvents which are easily removed, such ketones with at most 6 carbon atoms. The acylating agents are allowed to act until no more amino groups to be acylated can be traced. The dyestuffs according to the invention must also by isolated and dried with care, for example by salting out the alkali metal salts with sodium chloride in weakly acid solution and drying ata moderately raised temperature, preferably *in vacuo*.

Another process for the production of the metal-containing dyestuffs according to the invention consists in reacting metal-free dyestuffs of the general formula II with an agent introducing heavy metal of the atomic number 24-29. In this formula II XH is a metallisable group in o-position to the azo group and R, A, B, Y,

Z, m and n have the meanings given in formula I. Whilst observing the precautionary measures indicated in the first process mentioned with regard to the mobility of critical substituents, the metal-free dyestuffs are produced from components which contain at least one substituent Z as defined, or the radical containing the reactive substituent is introduced into dyestuffs which contain an acylatable amino group or a group which can be converted into such, this possibly after the modification into the acylatable amino group has taken place. In this process the compounds mentioned in the first process are used as acylating agents.

The usual agents giving off metal are used for the metallisation of the meal-free dyestuffs of the general formula II, for example mineral acid salts of copper, cobalt, nickel or chromium, advantageously in the presense of alkali metal salts of acetic acid or of polybasic oxygen acids of phosphorus as mineral acid buffering agents. The metallisation is performed at moderately raised temperatures and pH values of about 1-7 in order to prevent as far as possible too previous exchange of mobile substituents. The precautionary measures indicated above should also be taken when isolating and drying the dyestuffs.

The formazane compounds necessary as starting materials for the two above processes, for the production of which no protection is claimed, are obtained by methods known *per se*. For example they can be produced by the process described in the main patent of coupling 2 mols of aryl diazonium compound with 1 mol of a compound which can be coupled twice at a methylene or methine group possibly while splitting off substituents, or by the hydrazone method which is also described in the main patent. In this process 1 mol of an o-hydroxyaryl, o-carboxyaryl or o-di-sulphonylamidoaryl diazonium compound and 1 mol of an aryl diazonium compound not having such a metallisable group in the o-position are used or, in the hydrazone method the hydrazone and diazo components are so chosen that only one of them contains a metallisable substituent in the o-position to the hydrazo or diazo group.

As diazo components having a metallisable group in the o-position, principally those usual for the production of azo dyestuffs are employed, i.e., principally o-hydroxy- and o-carboxy-aminobenzenes and -aminonaphthalenes. These can be substituted by halogen, cyano, nitro, alkyl, aralkyl, cycloalkyl and aryl groups, by alkoxy, aryloxy, sulphonic acid, carboxylic acid, carboxylic acid ester, sulphonic acid ester, sulphonic acid alkyl-sulphonic acid aralkyl- or sulphonic acid arylamide groups, by alkylcarbonyl or arylcarbonyl, alkylsulphonyl or arylsulphonyl groups, by alkylamino, aralkylamino, cycloalkylamino or arylamino groups, by stilbylazo or arylazo groups and, finally, also by acylamino groups in which latter case, the acylamino groups are possibly saponified subsequently and, on completion of the dyestuff formation, converted into an amido group as defined. It is also possible to use those diazo components which, instead of the o-hydroxyl or o-carboxyl groups mentioned above, contain substituents which are not metallisable as such but after the coupling can be converted into metallisable groups. In particular ether groups, acyloxy groups and disulphonylamide groups are used as such.

The diazo components of the type mentioned above, in particular the o-carboxy- and o-disulphonylamidoaryldiazonium compounds can also be converted by reduction into the corresponding hydrazine compounds and then used as starting materials for the hydrazone production process.

As diazo components not having a metallisable group in the o-postion, also those compounds known from azo dyestuff chemistry are advantageously used. Examples of such are, aminobenzenes, aminonaphthalenes, aminoazoles such as, *e.g.*, 2-amino thiazoles, aminobenzthiazoles, 2-aminotriazoles, 4- or 5-aminopyrazoles, 3-aminoindazoles, also aminoazines such as; *e.g.*, 3- and 4-aminopyridines and 3- and 4-aminoquinolines, all of which may contain substituents of the type mentioned above. If the acylated or acylatable amino group as defined is present in one of these diazo components not having metallisable groups in the o-position, then it is advantageously an m- or p-monoacylaminobenzene diazonium compound possibly further substituted in the benzene nucleus, in particular it is an m- or p-monoacyl- or monoazinylamino- diazobenzene-o-sulphonic acid.

As coupling components which couple twice at a metaylene or methine carbon atom, possibly while splitting off substituents, principally the compounds described in the main patent are used, i.e., mainly α-carboxylalkanes and α-cyanoacetic acid esters or α-acylacetic acid esters, also, however, α-acylacetic acid arylamides.

Finally, principally aromatic-isocyclic aldehydes are used for the hydrazone formation as they lead to particularly valuable meso-aryl formazane dyestuffs. For example, benzaldehyde, tolualdehydes, 3-nitrobenzaldehydes, benzaldehyde-2,4-disulphonic acid, 2- or 4-chlorobenzaldehyde, 2,4-dichlorobenzaldehyde, anisaldehyde, vanillin, 4-dimethyl- or 4-dietnyl- amino- benzaldehyde and 4-dihydroxyethylaminobenzaldehyde are used. Also heterocyclic aldehydes such as, *e.g.*, furfurol, piperonal, pyridine, quinoline and benzimidazole aldehydes can be used, and finally, valuable end products are also obtained with aliphatic or araliphatic aldehydes such as, *e.g.*, acetaldehyde, croton-aldehyde, capronaldehyde, phenacetaldehyde or cinnamaldehyde.

A further process for the production of metal-containing dyestuffs according to the invention consists in starting from metallisable intermediate products of formazane compounds of the general formula II, first metallising these and only then forming the complete dyestuff. Such intermediate products, *e.g.*, correspond to the general formula III wherein XH, A and R have the meanings given in formula II.

These intermediates are obtained by coupling 1 mol of an aryldiazonium compound with a methylene or methine compound which, after the coupling at the methine C atom, also contain a carboxyl group or a substituent which can be converted into such a group such as, *e.g.*, a cyanic acid ester group or a carboxylic acid ester group. After the necessary convertion of such a substituent into the carboxyl group, the intermediate product of the above formula is treated with the agent giving off heavy metal and is then coupled with 1 mol of an aryldiazonium compound which contains at least one amino group as defined under Z in formula I, to form the metal-containing formazane dyestuff. The two components are always so chosen that in all there are at least one and not more than 5 strong acid, salt-forming groups present. It is possible to perform the metallisation and the second coupling in one single step. Diazo and azo components employed for this process have already been defined above as starting materials for the first two processes according to the invention.

The heavy metal-containing dyestuffs obtained by the process described are dark powders which, in the form of their alkali metal salts, dissolve very well in water. They are capable of penetrating natural and regenerated cellulose fibres very well and are suitable for the fast dyeing of these materials in red-brown, violet, blue-violet, blue, navy blue, green to grey shades. Advantageously the cellulose material is impregnated and printed at a low temperature, *e.g.*, at 20-50°C, with the possibly thickened dyestuff solution and the dyestuff is fixed by treating with acid binding agents. Natural and synthetic polyamide fibres are dyed advantageously in an acid bath or they are printed with neutral to weakly acid printing inks and the dyeings or prints are then treated with acid binding agents. Examples of such agents are sodium carbonate, potassium carbonate, di- and tri-sodium phosphate, caustic soda lye and, at temperatures over 50°C also sodium bicarbonate. Also the treatment with these agents can be performed even at room temperature or at a slightly raised temperature, often better results are obtained at an elevated temperature, *e.g.* at 70-160°C (advantageously after a mild intermediate drying of the impregnated or printed goods). Instead of an alkaline after-treatment, particularly when the dyestuffs are fixed hot, the acid binding agents advantageously in the form of alkali bicarbonates, can also be added to the impregnating liquors or printing pastes and then the dyeing is developed by a short heating or steaming at temperatures of over 100°C to 160°C. In this process, the addition of hydrotropic agents to the

printing inks and impregnating liquors is advantageous, *e.g.*, the addition of urea in amounts of 10-200 g per litre dyestuff.

The acid binding treatment chemically binds the new dyestuff to the fibres and, after soaping to remove non-fixed dyestuff, the cellulose dyeings attained therewith have excellent wet fastness properties and very good fastness to light. The dyeings are also very pure and level and have good fastness to rubbing

The following examples illustrate the invention. The temperatures are given therein in degrees Centigrade. Where not otherwise stated, parts are given as parts by weight and their relationship to parts by volume is as that of grammes to cubic centimetres.

Example 1.

The compound of formula V.

63.3 Parts of the copper complex compound of N-(2-hydroxy-3-aminophenyl-5-sulphonic acid)- N′ -(phenyl-2′,5′-disulphonic acid)-ms-phenyl formazane (obtained by coupling diazo-tised 6-acetylamino-2-amino-1-hydroxybenzene-4-sulphonic acid with the hydrazone from benzaldehyde and phenyl hydrazine-2,5-disulphonic acid, coppering and saponifying the acetylamino group) are dissolved in 1200 parts of water with a pH of 6.0 to 6.5. 21 Parts of β-chlorocratonic acid chloride in 100 parts of acetone are added dropwise to this solution within 1 hour at 45-50° and an aqueous solution of sodium carbonate is simultaneously added dropwise so that the reaction mixture always remains neutral. As soon as no more starting dyestuff can be traced, the dyestuff is precipitated with sodium chloride, filtered off, washed with sodium chloride solution and carefully dried *in vacuo*.

It is a dark powder which dissolves in warm water with a blue colour.

2 Parts of the dyestuff are dissolved in 4000 parts of water and 20 parts of sodium carbonate are added. 100 Parts of cotton are introduced at 40-45° and the dyebath is heated within 30 minutes to 80-85° and sodium chloride is simultaneously added so that at the end the content is 150 parts thereof per litre. Dyeing is continued for 1 hour at this temperature. The goods are then rinsed and soaped at the boil for 30 minutes. A fast blue dyeing is obtained.

Example 2.

The compound of formula VI.

63.3 Parts of the copper complex compound of N-(2-hydroxyphenyl-3,5-disulphonic acid)-N′-(4′-aminophenyl-2′-sulphonic acid)-ms-phenyl formazane (obtained by coupling equimolar amounts of diazotised 2-amino-1-hydroxybenzene-4,6-disulphonic acid and diazotised 4-acetylamino-1-aminobenzene-2-sulphonic acid in the presence of copper salts with phenyl formyl acetic acid ethyl ester by a known method and then saponifying the acetylamino group with dilute caustic soda lye), are dissolved with a neutral reaction in 1200 parts of water. This solution is added dropwise within 2 hours at 0-2° and at a pH of 2.0-2.5 to an aqueous, finely dispersed suspension of 22.2 parts of cyanuric chloride obtained by a pouring a solution of the cyanuric chloride in 150 parts of acetone into ice water. As soon as no more starting dyestuff can be traced, the dyestuff of the formula given above is precipitated by the addition of sodium chloride, filtered off, washed with dilute sodium chloride solution and finally dried *in vacuo*. The dyestuff dissolves in water with a blue colour.

Cotton is treated at 20° in a foulard with a 1 per cent solution of the new dyestuff with the addition of 15 parts of sodium carbonate per litre. The cotton is then rolled up and left for 2 hours at room temperature.

The goods are then rinsed, and soaped at the boil for 30 minutes. A beautiful, fast blue dyeing is obtained.

Further dyestuffs according to the invention are obtained by using the metal-containing amino formazane compounds given in columns II and III of the following Table and the acylating agents given in column IV thereof under the reaction conditions given in columns V and VI thereof according to the processes described in examples 1 and 2. The dyestuffs obtained dye cotton in the shades given in column VII of the Table.

Table 1.

I	II	III	IV	V	VI	VII
No.	amino formazane dyestuff	metal	acylating agent	acylating conditions pH	Temp.	shade on cotton
1.	N-(2-hydroxy-3-amino-phenyl-5-sulphonic acid)-N′-(phenyl-2′, 5′-disulphonic acid)-ms-phenyl-formazane.	Cu	2, 4, 5, 6-tetrachloropyrimidine	6·0—6·5	40—50°	blue
2.	N-(2-hydroxyphenyl-3, 5-disulphonic acid)-N′-(4′-aminophenyl-2′-sulphonic acid)-ms-phenylformazane.	Cu	5-methyl-2, 4, 6-trichloropyrimidine.	7·0—7·5	80—85°	Ditto.
3.	Ditto	Cu	2-ureido-4, 6-dichloro-1, 3, 5-triazine.	5·0—5·5	30—35°	Ditto.
4.	Ditto	Cu	2-methoxy-4, 6-dichloro-1, 3, 5-triazine.	Ditto	Ditto	Ditto.
5.	Ditto	Cu	chloromaleic acid anhydride .	6·5—7·0	30—35°	Ditto.
6.	N-(2-hydroxyphenyl-3, 5-disulphonic acid)-N′-(5′-aminophenyl-2′-sulphonic acid)-ms-phenylformazane.	Ni	β-chloropropionic acid chloride .	6·5—7·0	30—35°	violetty brown.
7.	Ditto	Ni	2, 6-dichloropyrimidine-4-carboxylic acid chloride.	Ditto	Ditto	Ditto.
8.	Ditto	Ni	chloroacrylic acid chloride . .	Ditto	Ditto	Ditto.
9.	N-(2-methylsulphonylaminophenyl)-N′-(4′-aminophenyl-2′-sulphonic acid)-ms-o-sulphonic acid phenylformazane.	Cu	2-(2′, 5′-disulphonic acid phenylamino)-4, 6-dichloro-1, 3, 5-triazine.	6·0—6·5	40—50°	blue.
10.	N-(2-methylsulphonyl-aminophenyl)-N′-(phenyl-2′, 5′-disulphonic acid)-ms-m-aminophenylformazane.	Cu	Ditto	Ditto	Ditto	Ditto.
11.	N-(2-hydroxyphenyl-3, 5-disulphonic N′-(4′-aminophenyl-2′-sulphonic acid)-ms-naphthyl-(1)-formazane.	Cu	2-(2′, 5′-disulphonic acid phenylamino)-4, 6-dichloro-1, 3, 5-triazine.	Ditto	Ditto	Ditto.
12.	N-(2-hydroxy-3-amino phenyl-5-sulphonic acid)-N′-(naphthyl-(1)-3′, 8′-disulphonic acid)-ms-phenylformazane.	Cu	2-ureido-4, 6-dichloro-1, 3, 5-triazine.	5·0—5·5	30—35°	grey.
13.	Ditto	C	2, 4, 5, 6-tetrachloropyrimidine	6·0—6·5	40—50°	Ditto.

Example 3.

The compound of formula VII, wherein R represents the 4,5,6-trichloropyrimidyl-(2)- or the 2,5,6-trichloropyrimidyl-(4)-radical.

26.9 Parts of 2-amino-1-hydroxybenzene-4,6-disulphonic acid are indirectly diazotised by the usual method. The suspension of the diazonium compound is added dropwise at 0.10° while stirring well to a suspension of 20.4 parts of phenylformyl acetic acid ethyl ester in 200 parts of water, 250 parts by volume of dioxan and 10.5 parts by volume of a 10 N-caustic soda lye solution in the presence of such amounts of calcinated sodium carbonate that after the addition of the diazonium compound, the reaction mixture has a weakly phenolphthalein alkaline reaction. On completion of the coupling the reaction is made weakly alkaline to brilliant yellow paper by the addition of concentrated hydrochloric acid, the mixture is diluted and boiled. After adding sufficient 10 N-caustic soda lye to ensure a strong alkaline reaction until the end of the saponification, the reaction product is refluxed for 10-20 minutes.

The solution of the saponification product is then made weakly acid to litmus paper with glacial acetic acid and a copper sulphate solution (corresponding to 7 parts of copper) is added. The mixture is then coupled at 0-10° with the diazonium salt obtained by diazotising 37 parts of the condensation product from 1,3-diaminobenzene-4-sulphonic acid and 2,4,5,6-tetrachloropyrimidine as described below.

18.8 Parts of 1,3-diaminobenzene-4-sulphonic acid are dissolved in 200 parts of water and the reaction is made neutral with sodium carbonate. 26.2 Parts of 2,4,5,6-tetrachloropyrimidine dissolved in 100 parts of acetone are added dropwise to this solution at 20-25° and simultaneously an aqueous trisodium phosphate solution is so added dropwise that the reaction mixture always has a neutral reaction. On completion of the reaction, the reaction product is precipitated with sodium chloride, filtered off, dissolved in 300 parts of water and diazotised at 0° with 25 parts of 30 per cent hydrochloric acid and 6.9 parts of sodium nitrite. The yellow suspension of the diazonium salt is made neutral to congo paper with sodium acetate.

After heating the reaction mixture to 45°, the isomeric mixture of the copper-containing dyestuffs of the formula VII, wherein R has the meaning defined hereinbefore, is precipitated by the addition of sodium chloride, filtered off, washed with sodium chloride solution and dried *in vacuo*. It is a dark powder which dissolves in water with a blue colour.

Cotton is treated in the foulard at 50° with a 1 per cent. solution of this dyestuff which also contains 20 parts of sodium carbonate and 200 parts of urea per litre. The impregnated goods are dried, then heated for 4 minutes at 140-160° and finally soaped at the boil for 30 minutes. A level blue dyeing is obtained which is fast to boiling.

Example 4.

The compound of formula VIII.

26.9 Parts of 2-amino-1-hydroxybenzene-4,6-disulphonic acid are indirectly diazotised by the usual method, coupled with 20.4 parts of phenylformyl acetic acid ethyl ester under the conditions described in example 3 and the ester group in the coupling product is saponified with dilute caustic soda lye.

The solution of the saponification product is then made neutral with acetic acid, treated with a solution of copper sulphate (corresponding to 7 parts of copper) and then coupled with the diazonium salt, the reaction of which has been made neutral, which is obtained by diazotising 28 parts of the condensation product from 1,4-diaminobenzene-2-sulphonic acid and β-chloropropionic acid chloride.

After heating to 45-50°, the copper-containing formazane complex of the above formula is precipitated by the addition of sodium chloride, filtered off, washed with sodium chloride solution and carefully dried *in vacuo*. It is a dark powder which dissolves in water with a blue colour.

If cotton is impregnated with a 2 per cent aqueous solution of this dyestuff thickened with sodium alginate, which solution contains 200 g. of urea and 20 g of sodium carbonate per litre, and after a mild drying the goods are steamed neutral for 5 to 10 minutes or are heated for 5 minutes at 130-150°, then soaped hot, rinsed and dried, a beautiful blue dyeing is obtained which is fast to washing.

Further dyestuffs according to the invention are obtained by the processes described in examples 3 and 4 using the metallising agents given in column II of the following Table 2 and the diazonium compounds given in column III thereof instead of the compounds mentioned above, which dyestuffs produce dyeings of the shades given in column IV.

Table 2.

I No.	II metallising agent	III diazonium compound from	IV shade of metal-containing formazane dyestuff on cotton
1.	nickel sulphate	1-amino-5-trichloropyrimidylamino-benzene-2-sulphonic acid.	violetty brown.
2.	copper sulphate	1-amino-5-dichloropyrimidylamino-benzene-2-sulphonic acid	blue.
3.	nickel sulphate	1-amino-5-dichloropyrimidylamino-benzene-2-sulphonic acid	violetty brown.
4.	copper sulphate	1-amino-5-β-chlorocrotonylamino-benzene-2-sulphonic acid	blue.
5.	nickel sulphate	Ditto	violetty brown.
6.	copper sulphate	1-amino-4-dichloropyrimidylamino-benzene-2-sulphonic acid	blue.
7.	Ditto	1-amino-4-(2′, 6′-dichloropyrimidine-4′-carbonylamino)-benzene-2-sulphonic acid.	blue.
8.	Ditto	1-amino-4-β-bromocrotonylamino-benzene-2-sulphonic acid	blue.
9.	Ditto	1-amino-4-(p-trichloropyrimidyl-aminophenyl)-benzene-2-sulphonic acid	blue.
10.	Ditto	1-amino-4-(p-dichloropyrimidylaminophenyl)-benzene-2-sulphonic acid	blue.

The following Table 3 contains further dyestuffs according to the invention having similar properties which are produced by using equivalent amounts of the components given in Columns II-V according to the processes fully described in example 3.

TABLE 3.

I No.	II metallising agent	III 1st diazonium compound from	IV coupling component	V 2nd diazonium compound from	VI shade of metal containing formazane dyestuff on cotton
1.	copper sulphate	N-(dimethylsulphonyl)-amino-2-aminobenzene.	acetoacetic acid anilide-2, 5-disulphonic acid.	1-amino-4-trichloropyrimidyl-aminobenzene-2-sulphonic acid.	brown violet.
2.	Ditto	Ditto	Ditto	1-amino-4-dichloropyrimidyl-aminobenzene-2-sulphonic acid.	Ditto.
3.	Ditto	Ditto	Ditto	1-amino-4-β-bromocrotonyl-aminobenzene-2-sulphonic acid.	Ditto.
4.	Ditto	2-amino-4-methylsulphonyl-1-hydroxybenzene-6-sulphonic acid.	phenylformyl acetic acid ethyl ester.	1-amino-4-trichloropyrimidyl-aminobenzene-2-sulphonic acid.	blue.
5.	Ditto	Ditto	Ditto	1-amino-4-dichloropyrimidyl-aminobenzene-2-sulphonic acid.	Ditto.
6.	Ditto	2-amino-4-methyl-sulphonyl-1-hydroxybenzene-6-sulphonic acid.	phenylformyl acetic acid ethyl ester.	1-amino-4-β-chloro-acrylyl-aminobenzene-2-sulphonic acid.	blue.
7.	Ditto	2-amino-1-hydroxybenzene-4, 6-disulphonic acid.	p-chlorophenylformyl acetic acid ethyl ester.	1-amino-4-trichloropyrimidyl-aminobenzene-2-sulphonic acid.	Ditto.
8.	Ditto	Ditto	Ditto	1-amino-4-dichloropyrimidyl-aminobenzene-2-sulphonic acid.	Ditto.

69 Parts of N-(2-carboxyphenyl-4-sulphonic acid)-N'-(4'-β - chloropropionylaminophenyl-2' - sulphonic acid)-ms-o-sulphonic acid phenylformazane (obtained by coupling diazotised 4-β - chloropropionylamino-1-aminobenzene-2-sulphonic acid with the hydrazone from benzal-dehyde-2-sulphonic acid and phenyl hydrazine-2-carboxylic acid-4-sulphonic acid by the known method), are dissolved with a neutral reaction in 1200 parts of water.

The dyestuff is converted into the corresponding copper complex compound by the addition of 150 parts of copper sulphate solution (corresponding to 7 parts of copper). The copper-containing dyestuff is then precipitated by the addition of sodium chloride, filtered off, washed with dilute sodium chloride solution and carefully dried *in vacuo*.

It is a dark powder which dissolves in water with a violet colour.

If cotton is impregnated with a 2 per cent. aqueous solution of this dyestuff thickened with sodium alginate which also contains 200 g of urea and 20 g of sodium carbonate per litre, and after a mild drying, the goods are steamed neutral for 5 to 10 minutes or heated for 5 minutes at 130-150°, soaped hot, rinsed and dried, then a blue-violet dyeing which is fast to washing is obtained.

If, in the process described in the above example, instead of the formazane compound from 4-β-chloropropionylamino-1-aminobenzene-2-sulphonic acid the metal-free formazane compounds obtained from the 4-trichloropyrimidyl- 4-dichloropyrimidyl- and 4-β-bromocrotonylamino- 1-aminobenzene-2-sulphonic acids are used, dyestuffs having similarly good properties are produced.

EXAMPLE 6.

The compound of formula VII wherein R represents the 4,5,6-trichloropyrimidyl-(2)- or the 2,5,6-trichloropyrimidyl-(4)-radical.

26.9 Parts of 2-amino-1-hydroxybenzene-4,6-disulphonic acid are indirectly diazotised by the usual method and coupled with 20.4 parts of phenylformyl acetic acid ethyl ester under the conditions given in example 3.

After adding sufficient caustic soda lye to ensure a strong alkaline reaction until the end of the saponification, the coupling product is refluxed for 10 minutes.

The solution of the saponification product is then made acid to litmus paper with glacial acetic acid and is coupled with the neutralised diazonium salt obtained by diazotising 37 parts of the condensation product of 1,4-diaminobenzene-2-sulphonic acid and 2,4,5,6-tetrachloropyrimidine at 0-10°.

A copper sulphate solution (corresponding to 7 parts of copper) is then added to the coupling mixture. After heating for a short time at 45°, the isomeric mixture of copper-containing dyestuffs of the formula VII wherein R has the meaning as hereinbefore defined is precipitated by the addition of sodium chloride, filtered off, washed with sodium chloride solution and carefully dried *in vacuo*. It is a dark powder which dissolves in water with a blue colour.

If cotton is impregnated with a 2 per cent. aqueous solution of this dyestuff thickened with sodium alginate which also contains 200 g of urea and 20 g of sodium bicarbonate per litre and, after a mild drying, the goods are steamed neutral for 5 to 10 minutes or are heated for 5 minutes at 130-150°, soaped hot and then rinsed and dried, a beautiful, blue dyeing which is fast to washing is obtained.

EXAMPLE 7.

2 Parts of the dyestuff obtained according to example 4 are dissolved in 5000 parts of water at 40° and then 0.5 parts of a non-ionogenic dispersing agent, for example the condensation product from 25 mols of ethyleneoxide and 1 mol of octadecyl alcohol or octadecylamine, and 6 parts of acetic acid and finally 0.5 parts of a polyquaternary ammonium compound, e.g., the condensation product from 11.5 parts of N, N', N''-pentamethyldiethylene-triamine and 14.3 parts of β,β'-dichlorodimethyl ether are added. 100 Parts of wool are entered into the dyebath so prepared, the bath is brought to the boil within 30 minutes and dyeing is continued for 1 hour at this temperature. 4 Parts of 25 per cent ammonia are then added to the dyebath and the bath is boiled for another 30 minutes. The goods are then rinsed, 3 parts of 85 per cent formic acid to 100 parts of water being added to the last rinsing bath. A level, blue dyeing which has good fastness properties is obtained.

We claim:

1. Process for the production of metal-containing reactive dyestuffs of the general formula I of the accompanying drawings, wherein R represents a monovalent

aromatic-isocyclic or aromatic-heterocyclic or araliphatic radical, a nitro-cyano-, carboacyl- or aryl-carbonylamino group.

A and B each represent the radical of a diazo component,

X represents a metal binding group in o-position to the azo linkage,

Y represents the sulphonic acid group, the carboxyl group, the phosphonic acid group or an acylated sulphamide group,

Z represents a 2,4-dihalogen-1,3,5-triazinyl radical, a 2-alkoxy-, 2-alkyl-, 2-aryl-, 2-amino-, 2-alkylamino-, 2-arylamino-, 2-ureido-, 2-guanidino-4-halogen-1,3,5-triazinyi-(6)-radical, a 2,4- or 4,6-dinalogenpyrimidyl radical possibly substituted in 5-positin by a halogen atom, a nitro, acyl, cyano, alkyl, or aryl group, a 2,6-dihalogenpyrimidyl-4-carbonyl group, a β-halogen-alkanoyl, a β-halogenalkanoyl or a β-halogenalkylsulphamylbenzoyl radical, bound to A or B by way of a primary or secondary amini group or aminobenzoylenamino group,

Me represents a heavy metal of the atomic numbers 24-29,

n represents a positive whole number from 1-5, and

m represents a positive whole number of at most 2,

characterised by reacting dyestuffs of the formula I in which A and B represent radicals of diazo components with an acylatable primary or secondary amino group or an acylatable aminobenzoylenamino group with an acylating agent introducing the substituent Z, the reaction being performed at pH values of about 2-7.

2. Modification of the process according to Claim 1 for the production of metal-containing reactive dyestuffs of the general formula 1 defined in Claim 1 characterised by reacting dyestuffs of the general formula II wherein

XH represents a metallisable group in o-position to the azo group, and the other symbols R, A, B, Y, Z, n and m have the meanings given in Claim 1,

with an agent giving off heavy metal of the atomic numbers 24 to 29.

3. Modification of the process according to Claim 1 for the production of metal-containing reactive dyestuffs of the general formula I defined in Claim 1 characterised by treating a metallisable intermediate product of the general formula III wherein

XH represents a metallisable group in o-position to the azo group and the other symbols R and A have the meanings given in Claim 1.

first with an agent giving off heavy metal of the atomic numbers 24-29 and then coupling the reaction product with an aryl diazonium compound which contains at least one group of the meaning given under Z in Claim 1 to form the metal-containing formazane dyestuff, the heavy metal containing reaction product and the diazonium compound being so chosen that the sum of the strongly acid, salt-forming water solubilising substituents is at least 1 and not more than 5.

4. Process according to Claims 1 and 3 characterised by the use of those halogen azine compounds as acylating agents which, in a six-members heterocyclic compound of aromatic character, contain at least 2 tertiary ring nitrogen atoms and at least 2 halogen atoms of the atomic numbers 17 and 35 at ring carbon atoms adjacent thereto.

5. Process according to Claims 1, 3 and 4 characterised by the use of trihalogen pyrimidines or tetrahalogen pyrimidines as acylating agents.

6. Process according to Claims 2 and 3 characterised by the use of those dyestuffs or dyestuff components which contain an amido group derived from a β-halogen fatty acid.

7. Process according to Claims 2 and 3 characterised by the use of dyestuffs or dyestuff components of the general formula II or III which contain as group Z a 2,4-dihalogen-1,3,5-triazinyl radical, a 2-alkoxy- 2-alkyl-, 2-amino-, 2-alkylamino-, 2-arylamino-, 2-ureido-, 2-guanidino-4-halogen-1,3,5-triazinyl-(6)-radical, a 2,4- or 4,6-dihalogenpyrimidyl radical possibly substituted in 5-position by a halogen atom, a nitro, acyl, cyano, alkyl or aryl group or a 2,6-dihalogen-pyrimidyl-4-carbonyl group bound to A or B by way of a primary or secondary amino group.

8. Process according to Claims 2, 3 and 7 characterised by the use of dyestuffs or dyestuff components of the general formula II or III which as group Z contain a 2,4- or 4,6-dihalogenpyrimidyl radical substituted in 5-position by a halogen atom bound to A or B by way of primary or secondary amino group.

9. Process according to Claims 1 to 8 characterised by the use of dyestuffs or dyestuff components of the general formulae I, II or III, containing copper or nickel or of agents giving off such heavy metals.

10. Process according to Claims 1-3 characterised by the use of dyestuffs or dyestuff components of the general formulae I, II or III, which as group R contain a radical of the benzene or naphthalene series.

11. Dyestuffs of the general formula I of the drawings, wherein R represents a monovalent aromatic-isocyclic or aromatic-heterocyclic or araliphatic radical, a nitro-cyano-, carbacyl- or aryl-carbonylamino group,

A and B each represent the radical of a diazo component,

X represents a metal binding group in o-position to the azo linkage,

Y represents the sulphonic acid group, the carboxyl group, the phosphonic acid group or an acylated sulphamide group,

Z represents a 2,4-dihalogen-1,3,5-triazinyl radical, a 2-alkoxy- 2-alkyl-, 2-aryl-, 2-amino-, 2-alkylamino-, 2-arylamino-, 2-ureide-, 2-guanidino-4-halogen-1,3,5-triazinyl-(6)-radical, a 2,4- or 4,6-dihalogen-pyrimidyl radical possibly substituted in 5-position by a halogen atom, a nitro, acyl, cyano, alkyl, or aryl group, a 2,6-dihaiogenpyrimidyl-4-carbonyl group, a β-halogenalkanoyl, a β-halogenalkenoyl or a β-halogenalkylsulphamylbenzoyl radical, bound to A or B by way of a primary or secondary amino group or aminobenzoyleneamino group,

Me represents a heavy metal of the atomic number 24-29,

n represents a positive whole number of 1 to 5, and

m represents a positive whole number of at most 2,

whenever prepared by the process claimed in any of Claims 1 to 10.

12. Dyestuffs according to Claim 11 wherein Z has the meaning given in Claim 7 or it represents a β-halogen-alkanoyl or a β-halogenalkenoyl radical bound to A or B by way of a primary or secondary amino group.

13. Dyestuffs according to Claim 11 wherein R, A and B represent radicals of the benzene or naphthalene series, Y represents the sulphonic acid group and Me represents copper or nickel.

14. Process for the manufacture of metal-containing reactive dyestuffs according to Claim 11 substantially as described with reference to any of the forgoing Examples 1 to 6.

15. Metal-containing reactive dyestuffs according to Claim 11 whenever prepared or produced by the process of manufacture particularly described.

16. A metal-containing reactive dyestuff according to Claim 11 as identified in any of the foregoing Examples 1 to 6 including a dyestuff resulting from an alternative reactant specified in the Tables, whenever prepared by the process claimed in any of Claims 1 to 10.

17. Dyed or printed textile material whenever produced by applying to such material dyestuffs as defined in any of Claims 11 to 13 whenever prepared by the process claimed in any of Claims 1-10.

18. Dyed cellulose fibres whenever produced by applying to such fibres dyestuffs as defined in any of Claims 11 to 13 whenever prepared by the process as claimed in any of Claims 1-10, substantially as described in Example 1 to 6.

R. HALL,
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Agent for the Applicants.
Dated this 29th day of December 1960.

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NO/: 74730 of 1960.

2 Sheets
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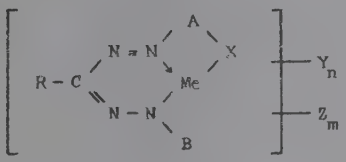

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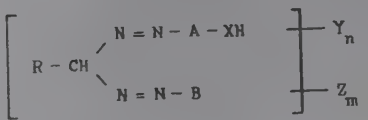

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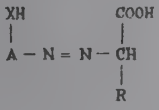

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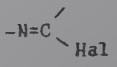

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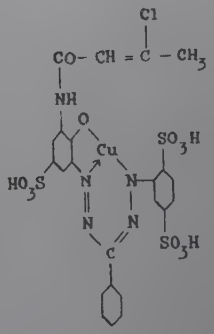

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NO/ 74730 of 1960

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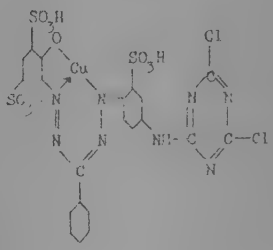
Sheet 2.

VI



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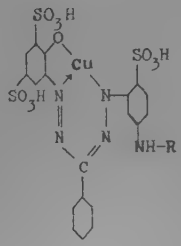

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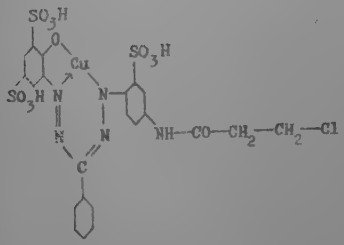

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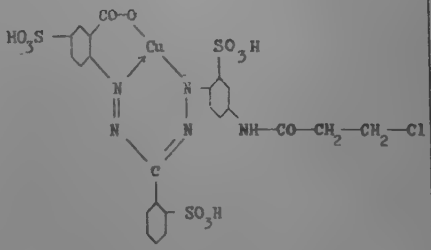

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Specification No. 74732, filed 29th December 1960/8 Paus 1882 (Saka).

(Accepted 5th December 1961.)

"IMPROVEMENTS IN PUMPS, AND IN PARTICULAR FUEL INJECTION PUMPS, HAVING OPPOSED PISTONS AND A ROTARY DISTRIBUTING VALVE ELEMENT."

PIERRE ETIENNE BESSIERE, ENGINEER, OF 55, BOULEVARD COMMANDANT CHARCOT, NEUILLY-SUR-SEINE (SEINE), FRANCE, OF FRENCH NATIONALITY.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

The present invention relates to self-regulating pumps, especially for the feed of fuel to internal combustion engines, of the type comprising a first part, which is fixed, and a second part rotating with respect to said first part and acting as a distributing valve element having an outlet adapted to come in communication, during the rotation of said second part, successively with a plurality of delivery means, one of these two parts carrying a cam and the other a pair of opposed cylinders, with pistons slidable in said cylinders respectively and operatively connected with said cam to be reciprocated by it, this last mentioned part being provided with a delivery conduit adapted to connect said cylinders, during the delivery strokes of the pistons therein, with said distributing valve element outlet as it is in communication with one of said delivery means.

In prior patents and patent applications, I already described pumps of this kind wherein said regulation is obtained by means of a movable member called "shuttle" which, during the delivery strokes of the pump piston, is driven, to effect its own outward stroke, by a liquied delivered by this piston or preferably by an auxiliary piston working in synchronism with the pump piston, and which, at the end of its outward stroke, opens a discharge conduit for the liquid which is driving said shuttle, so as to stop fuel injection to the internal combustion engine whereas the return stroke of the shuttle is produced, between two consecutive delivery strokes of the pump piston, by a spring, these return strokes being braked by the fact that the shuttle, during said return strokes, must force at least a portion of the liquid by which its outward stroke had been produced through a throttled passage which is preferably adjustable. Due to this braking of the return stroke of the shuttle and for speeds of rotation of the pump exceeding a given value (i. e. for speeds of the engine fed by the pump also exceeding a given value) the shuttle on its return stroke has not yet reached, when the next delivery of the pump begins, its position of rest, determined by an abutment against which the above mentioned spring tends to apply it at the end of its return stroke. In this case, the shuttle is compelled to start back on its next outward stroke after an incomplete return stroke, which is the shorter as the speed increases beyond the above mentioned given value. This produces a corresponding reduction of the amount of fuel injected into the engine during every cycle of the pump. The phenomenon thus produced to ensure regulation of the pump is called "liquid abutment".

The object of the present invention is to provide a pump having opposed pistons and a rotary distributing valve element as above mentioned with regulating means based on said liquid abutment phenomenon.

For this purpose, according to my invention, the fixed part is provided with a cylindrical housing in which is slidably mounted a shuttle piston which during each of said delivery strokes is driven, on its outward strokes, by liquid delivered either by said pistons or, preferably, by auxiliary pistons moving in synchronism with said pistons, said shuttle, at the end of every outward stroke thereof, opening a discharge conduit for said liquid in such manner as then to stop the flow of fuel through said delivery conduit, the return strokes of said shuttle, which take place during the intervals between consecutive delivery strokes of the pump pistons, being produced by a spring, and being braked by the fact that the shuttle, during said return strokes, must force through a throttled passage at least a portion of the liquid which had previously driven it on its outward stroke, whereby, for speeds of rotation of the pump above a given value the outward strokes of the shuttle become shorter and shorter as this speed increases, and consequently fuel flow through the delivery conduit is stopped after a shorter and shorter portion of the delivery strokes of the pump pistons.

Preferred embodiments of the present invention will be hereinafter described with reference to the accompanying drawings, given merely by way of example and in which :

Fig. 1 is a diagrammatic axial sectional view of a pump made according to a first embodiment of the present invention, the parts being shown in the position corresponding to the end of a delivery stroke of the pistons.

Figs. 2 and 3 are longitudinal sectional views of the pump of Fig. 1 respectively in the relative positions of the parts corresponding to fuel delivery and to suction.

Figs. 4 and 5 are diagrammatic axial sectional views of two pumps made according to a second embodiment and a third embodiment respectively of the invention.

In the embodiment of Figs. 1 to 3, the pump comprises on the one hand a fixed part 1 which carries cam 2 of annular shape and on the other hand a rotating part 3 acting as a distributing valve element. Parts 3 is provided with a radial recess 4, forming two opposed cylinders, in which are slidable opposed pistons 5. A push-piece 6 provided with a roller 7 is interposed between cam 2 and each of the pistons 5. The working space 8, which is limited, in recess 4, by the two pistons 5, is in permanent communication with a conduit 9 extending longitudinally in rotating part 3. This conduit 9 serves both to suck in fuel from a feed chamber 10 through channel 11 provided in fixed part 1 and radial channels 12 provided in rotating part 3 and to deliver fuel toward fuel injectors (not visible on the drawings) through connecting members such as 13 provided with check valves 14, radial channels such as 15 provided in fixed part 1 and a radial channel 16 provided in rotating part 3 which thus works as a distributing valve element. Chamber 10 is fed with fuel from a feed pump 17 driven by rotating part 3, this feed pump being preferably a gear pump as shown.

Fixed part 1 is provided with a discharge conduit 18 arranged to be in communication with delivery conduit 9 during the delivery strokes of opposed pistons 5, this discharge conduit 18 being controlled by a shuttle member 19 adapted to work according to the so-called liquid abutment phenomenon.

For this purpose, rotating part 3 is provided with radial channels 20, permanently in communication with delivery conduit 9 and adapted to connect said conduit with discharge conduit 18 every time delivery conduit 9 is in communication with one of the fuel injectors through channels 15 and 16.

Shuttle 19 is operated by the following means.

Every piston 5 carries, integral therewith an auxiliary piston 5a of larger diameter sliding in a corresponding cylinder formed in part 3 so as to form two variable volume working chambers 21. These chambers 21 are connected to a common channel 22 which, during every delivery stroke of main piston 5, is placed in communication, through longitudinal groove 23 provided in the periphery of rotary part 3 and a channel 24 provided in fixed part 1, with a chamber 25 limited by one of the end faces of shuttle 19 (Fig. 2). On the other hand, this channel 22, during every suction stroke of main piston 5, is placed in communication, through channel 26 provided in rotary part 3 and channel 27 provided in fixed part 1, with feed chamber 10 (Fig. 3). Thus, during every delivery stroke of main piston 5, shuttle 19 moves on its outward stroke (toward the right hand side of Fig. 2) under the action of the liquid delivered by auxilary piston 5a. The end of this outward stroke of the shuttle is determined by the fact that this shuttle clears an outlet conduit 28, said shuttle then also clearing, through its groove 19a, discharge conduit 18. During the suction stroke of the main piston 5 (Fig. 3), shuttle 19 moves on its return stroke under the action of a ruturn spring 29 but this movement is braked by the fact that the shuttle must force the liquid precedingly admitted into chamber 25 to flow through throttled passage 30 which is preferable adjustible by means of a screw 31. This is due to the fact that, during said return strokes of the shuttle, chamber 25 is on the one hand cut off from channel 22 due to the displacement of groove 23 and on the other hand placed in communication with a channel 32, which contains throttle passage 30, through a longitudinal groove 33 and an annular groove 34 provided in rotating part 3. Consequently when the speed of rotation of the pump is above a given value, shuttle 19 before reaching his position of rest which is determined by an abutment 35, is struck by a jet of fuel delivered by auxiliary pistons 5a, which starts a new outward stroke of the shuttle. This outward stroke is therefore shortened, so that the time at which the shuttle clears discharge passage 18 occurs earlier during every cycle of the pump. Thus the amount of fuel delivered by main pistons 5 through delivery conduit 9 is reduced.

Annular cam 2 may be adjustable angularly with respect to fixed part 1 so as to vary the advance of injection. Furthermore the front edge of the groove 19a of shuttle 19 may be inclined, as shown at 19b, so that an angular adjustment of the shuttle, effected for instance by acting on a square portion 36 thereof, permits of varying the amount of fuel delivered on every cycle of the pump.

In the embodiments of Figs. 4 and 5, cam 2 is carried by the rotating element 3 and the opposed pistons 5 are reciprocable in fixed part 1.

In the construction of Fig. 4, cam 2 is annular and the portion of rotating part 3 which acts as a distributing valve is of tabular shape. In this portion is engaged a cylindrical extension 1a of fixed part 1 through which extends delivery conduit 9. In Fig. 4, the same reference numerals have been used to designate elements having the same functions as the corresponding elements of Figs. 1 to 3. These two embodiments (Fig. 4 and Figs. 1-3) differ essentially by the fact that in the construction of Fig. 4 a spring 37 must be provided to urge piston 5 away from each other, whereas such a spring is not necessary in the construction of Figs. 1-3, where the centrifugal force plays the same part as this spring. Furthermore in the construction of Fig. 4 where conduit 9 is provided in fixed part 1, this conduit is permanently in communication with the groove 19a of shuttle 19. Finally there must be provided, between chamber 25 and channel 22 which communicates with the two variable volume chambers 21 of auxiliary piston 5a, a check valve 38 which compels the liquid forced out by the shuttle to pass through throttled passage 30. Fixed part 1 may be adjusted angularly with respect to the pump frame 39 so as to vary the advance of injection.

According to the embodiment of Fig. 5, cam 2 is a solid rounded cam and pistons 5 are disposed on opposite sides of this cam so that it is necessary to provide two return springs 37a and 37b and two distinct working spaces 8a and 8b, which are connected together by channel 40 and a groove 41 of rotating part 3. This groove is in permanent communication with delivery conduit 9 which, as in the case of Figs. 1 to 3, is provided in rotating part 3. The feed chamber analogous to those shown at 10 in Figs. 1 and 4 is not visible in Fig. 5 and it is connected, through channels 11 and grooves 12a pleying the same part as the channels 12 of Figs. 1 to 4, with delivery conduit 9. Likewise, grooves 16a play the same part as the distribution channels 16 of Figs. 1 to 4. The variable volume chambers 21 of auxiliary piston 5a are connected together by channels 42, longitudinal grooves 23a analogous to grooves 23 of Figs. 1, 2, 3 and annular grooves 43 provided in rotating part 3, said grooves being in permanent communication, through channel 24, with the chember 25 of the shuttle. Finally, longitudinal grooves 33a, communicating with said grooves 43, play a part analogous to that of the longitudinal groove 33 of Figs. 1 to 3.

As the elements of the pump of Figs. 4 and 5 are analogous to those of the pump of Figs. 1 to 3 or perform analogous functions, it is unnecessary to describe the operation of the pump of Figs. 4 and 5.

I CLAIM :—

1. A self regulating pump, especially for the feed of fuel to an internal combustion engine, comprising a first part which is fixed, and a second part rotating with respect to said first part and acting as a distributing valve element having an outlet adapted to come in communication, during the rotation of said second part, successively with a plurality of delivery means, one of these two parts carrying a cam and the other a pair of opposed cylinders, with pistons slidable in said cylinders respectively and operatively connected with said cam to be reciprocated by it, this last mentioned part being provided with a delivery conduit adapted to connect said cylinders, during the delivery strokes of the pistons therein with said distributing valve element outlet as it is in communication with one of said delivery means, this pump being characterized in that said fixed part is provided with a cylindrical housing in which is slidably mounted a shuttle piston which during each of said delivery strokes is driven, on its outward strokes, by liquid delivered either by said pistons or, preferably, by auxiliary pistons moving in synchronism with said pistons, said shuttle, at the end of every outward stroke thereof, opening a discharge conduit for said liquid in such manner as then to stop the flow of fuel through said delivery conduit, the return strokes of said shuttle, which take place during the intervals between consecutive delivery strokes of the pump pistons, being produced by a spring, and being braked by the fact that the shuttle, during said return strokes, must force through a throttled passage at least a portion of the liquid which had previously driven it on its outward stroke, whereby for speeds of rotation of the pump above a given value, the outward strokes of the shuttle become shorter and shorter as this speed increases, and consequently fuel flow through the delivery conduit is stopped after a shorter and shorter portion of the delivery strokes of the pump pistons.

2. A pump according to claim 1, wherein said delivery conduit is in communication with said discharge conduit so that opening of said discharge conduit by the shuttle immediately stops the flow of fuel through said delivery conduit.

3. A pump according to either of claims 1 and 2, wherein the cam is of annular shape and carried by the fixed part and the opposed cylinders and pistons are located in the rotating part.

4. A pump according to either of claims 1 and 2, wherein the cam is carried by the rotating part and the opposed pistons and cylinders are located in the fixed part.

5. A pump according to claim 4, wherein the cam is annular and the rotating part which carries it includes a por-

tion in the form of a tubular extension in which is engaged a cylindrical portion of the fixed part, in which is provided the delivery conduit.

6. A pump according to claim 4, wherein the cam is a solid cam having a rounded outline and the pump pistons are disposed on opposite sides of this cam, the delivery conduit being provided in the rotating part.

7. A pump substantially as hereinabove described and illustrated by the appended drawings.

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Agent for the Applicants.

Dated this 29th day of December 1960.

Printed by The Nelys Printing Works, Calcutta-1.

P. E. BESSIERE.
No. 74732 of 1960.

(2 Sheets)

Sheet 1.

Fig. 1.

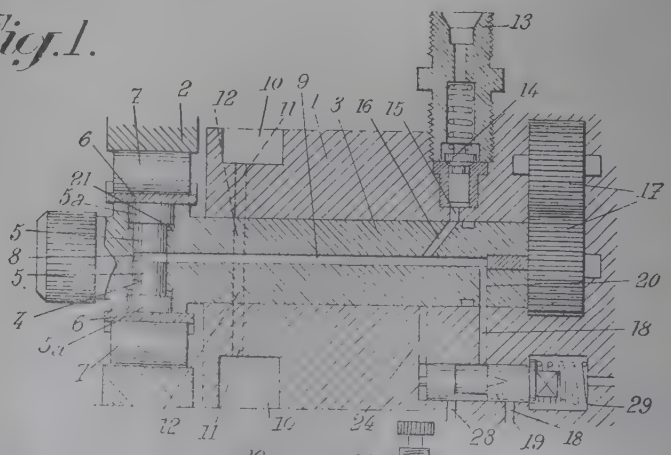

Fig. 2

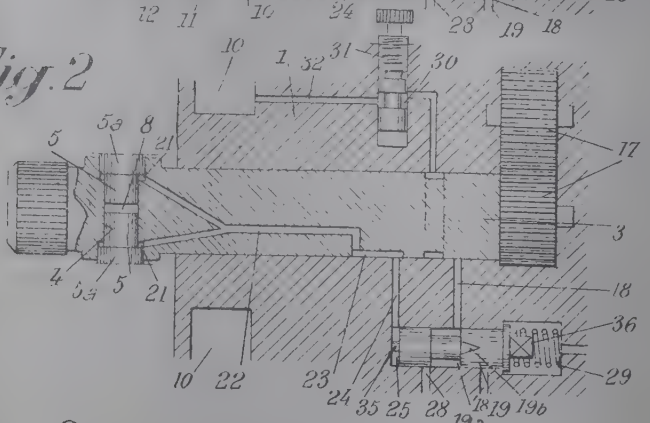

Fig. 3.

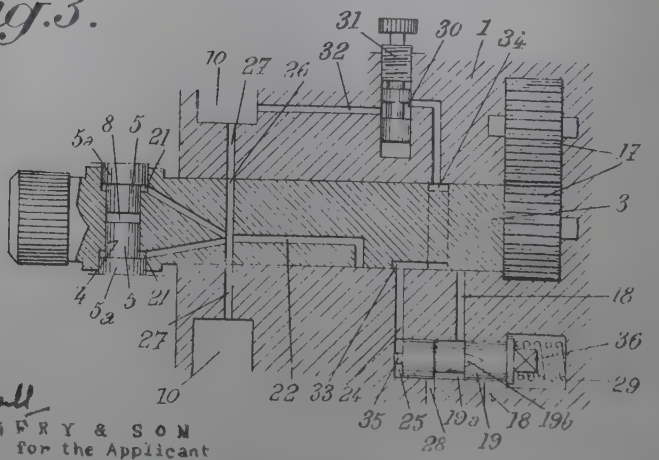

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Fig. 4

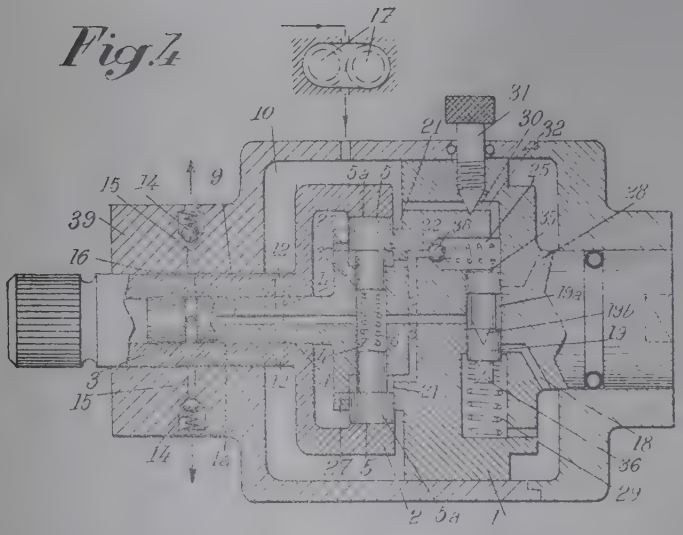
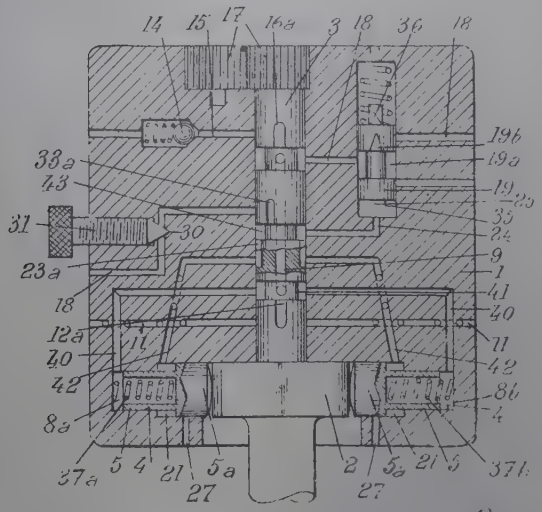


Fig. 5



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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.
Specification No. 74733, 29th December 1960. (Pausa 1882 Saka.) (Accepted 7th April 1962.)

IMPROVEMENTS IN AND RELATING TO ARTICULATED VEHICLES.

CAMPBELL & McGILL LIMITED, of Easton Lane, Winchester, Hants., Hampshire, England, a British Company.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to vehicles including a tractor and a trailer unit and more especially to steering mechanism for effecting articulated movement of the units.

According to the present invention steering mechanism for effecting a turning movement of a trailer relative to a tractor, comprises a vertically disposed king pin rotatably mounted on the tractor and adapted to have a towing arm or the like of a trailer connected thereto, means for rotating the king pin comprising an arm mounted on the tractor for rotation about a locus spaced from the king pin along the longitudinal axis of the tractor, the arm extending laterally of the king pin and being connected thereto by a pivoted link, the arm and link being so arranged that a predetermined rotation of the arm about the said locus will effect a substantially greater rotational movement of the king pin to impart a steering movement.

The locus of the arm may be disposed forwardly of the king pin, and the link pivoted at one end to the said arm and at the other end to a member secured to the king pin and extending rearwardly thereof, such that the pivotal connection of the link to said member is spaced rearwardly of the king pin.

Alternatively the locus point of the arm may be disposed rearwardly of the king pin, and the link pivoted at one end to said arm and at the other end to a member secured to the king pin and extending forwardly thereof, such that the pivotal connection of the link to said member is spaced forwardly of the king pin.

To enable the invention to be fully understood it will now be described with reference to the accompanying drawings in which :—

Figure 1 is a side view of an articulated vehicle according to one embodiment of the invention.

Figure 2 is a plan view thereof.

Figure 3 is a plan view showing the tractor and trailer units turned relatively to one side of the normal fore and aft position.

Figure 4 is a side view showing the trailer in load tipping position.

Figure 5 is a side view, on an enlarged scale, illustrating the steering mechanism.

Figure 6 is a plan view of the steering mechanism.

Figure 7 is a fragmentary sectional view showing the mounting of the tubular post and drive shaft.

Figure 8 is an elevation taken in the direction of arrow *a* of Figure 7.

Figure 9 is a plan view of a clamping block for securing the drive shaft 13 to the member 10.

Figure 10 is a side view of an articulated vehicle according to a modification of the invention.

Figure 11 is a plan view thereof.

Figure 12 is a plan view showing the tractor and trailer units turned relatively to one side of the normal fore and aft position.

Figure 13 is a side view showing the trailer in load tipping position.

Figure 14 is a fragmentary sectional view showing the mounting of the king pin.

Figure 15 is a plan view of the steering mechanism and

Figure 16 is a side view, on an enlarged scale, illustrating the steering mechanism.

As shewn in Figs. 1 to 9 of the accompanying drawings, A comprises tractor unit and B a load carrying trailer unit. The tractor unit comprises a frame 1 supported on driving wheels 2 which are driven through suitable gearing by an engine housed under the bonnet 3.

The trailer unit includes a body 4 for carrying sand, gravel, stone or any other load, the body being supported on wheels 5. A frame 6 is provided including two side members 7 each having its rear end pivotally connected to a lateral stud 8 on the side of the body and its forward end integrally connected to a tow arm 9 which, as shown more particularly in Figure 7, has a tubular member 10 integral with its forward end.

The frame of the tractor unit includes a rigid beam 11 of box section to which a tubular vertically extending post 12 is rigidly secured as by welding. A king pin or drive shaft 13 is rotatably mounted in the post 12 and as shown, bronze bearing bushes 14, 15, are provided at the upper and lower ends of the post and king pin. The tubular member 10 of the tow arm 9 is rotatably mounted on the post 12 and bronze bearing bushes 16, 17 and a bronze thrust pad 18 are provided.

The upper end of the tubular member 10 has castellations and is drivingly connected to the king pin 13 by a block 19 having segments 19*a* engaging the castellations and keyways 20 engaging in keys 21 on the king pin 13. As the king pin 13 is positively connected to the tubular member 10 of the tow arm 9, rotation of the king pin will produce a corresponding rotation of the tow arm to impart a turning movement to the trailer unit B to steer the vehicle.

The means for rotating the king pin 13 is best shown in Figures 5 and 6 and as shown a quadrant 22 is keyed to the lower end of the king pin and at a position spaced rearwardly thereof, a pair of links 23, 24 are pivoted, one link extending laterally of each side of the quadrant. The outer ends of the respective links are pivoted to swinging arms 25, 26 of L-like shape, the opposite ends of these arms having apertures through each of which extends a fulcrum pin 27 secured to the rigid beam 11 on the tractor frame a predetermined distance forwardly of the king pin 13.

Intermediate their ends the arms 25, 26 are respectively connected by pivot pins 28, 29 to eyes 30, 31 connected with the cylinders 32, 33 of hydraulically operated rams, the piston rods 34, 35 of which are connected to a fixed cross head 36 on the beam 11 of the tractor.

The rams are provided with control valves 37, 38 so arranged that when moved axially of the ram cylinder, in either a forward or rearward direction, they will control the supply of hydraulic fluid under pressure to effect an axial movement of the cylinders in the same direction.

It will be noted that the respective rams are mounted on opposite sides of the tractor frame and connected with the swinging arms on opposite sides of the link system. Both rams are adapted to be operated simultaneously but in opposite directions in such a manner that one ram imparts a pushing movement to its connected swinging arm, and the other ram imparts a pull to its connected swinging arm such that both rams combine to effect the rotation of the link means about the locus defined by the pin 27.

The simultaneous operation of the rams is obtained by means of a pair of bell crank levers coupled by a transfer link. As shown, a cross link 39 is provided having its opposite ends respectively pivoted to the pins 28, 29 the cross link is not connected with the fulcrum pin 27 but is formed with a medial recessed portion 40 through which the fulcrum pin 27 extends freely. Bell crank levers 41, 42 are pivoted at 41*a*, 42*a* to the cross link. One arm of the bell crank 41 is pivoted to a link 43 connected with the ram control valve 37 and one arm of the bell crank 42 is pivoted to a link 44 connected with the ram control valve 38, the other arms of the two bell cranks being pivoted to the opposite ends of a transfer link 45.

The control valve 38 is adapted to be actuated by a drag link 46 operated by rotation of the steering wheel 47

of the tractor. The drag link is pivoted to an L-shaped link 48 which is connected at its elbow with the control valve 38. To limit the movement of the link 48 to a rectilinear sliding movement and prevent any tendency for it to rotate about the control valve, the free end of the arm 49 of the link 48 is pivoted to one end of a control arm 50 whose other end is pivoted to the frame of the tractor.

In operation if it is desired to steer the vehicle to make a right hand turn, the appropriate rotation of the steering wheel 47 will be transmitted through the steering box to drag link 46 to displace it rearwardly. The arm 48 is accordingly moved rearwardly to actuate the control valve 38 in a rearward direction and fluid under pressure controlled by the valve effects a rearward movement of the ram cylinder 33 to exert a pushing action on the swinging arm 25.

By reason of the interconnected bell crank levers 41, 42 the control valve 37 is simultaneously actuated but in this case it is given an axial sliding movement in a forward direction and the ram cylinder 32 moves in the opposite direction to the ram cylinder 33 and exerts a pull on the swinging arm 26. The combined action of the rams 32, 33 is to impart a rotational movement to the link system to turn it in a counter-clockwise direction about the fulcrum pin 27.

The rotational movement is transmitted through the links 23, 24 and quadrant 22 to the king pin 13. As the drive shaft is keyed to the tubular member 10 on the tow arm 9, a torque is applied to the tow arm and a reaction torque to the tractor such that tractor is turned to the right relatively to the trailer as indicated in Figure 3 of the drawings.

It will be understood that if desired a single and larger capacity hydraulic ram could be used in place of the two smaller rams and in this case only one swinging arm would be necessary. The provision of two opposed rams as described has however advantages over a single ram.

As shown in Figs 10 to 16 of the accompanying drawings the vehicle includes a tractor unit A and a load carrying trailer unit B. The tractor unit comprises a frame 1 supported on driving wheels 2 which are driven through suitable gearing by an engine housed under the bonnet 3.

The trailer unit includes a body 4 for carrying sand, gravel, stone or any other load, the body being supported on wheels 5. A frame 6 is provided including two side members 7 each having its rear end pivotally connected to a lateral stud 8 on the side of the body and its forward end integrally connected to a tow arm 9 which, as shown more particularly in Figures 14 and 16, has two connecting members 10 integral with its forward end.

The frame of the tractor unit includes a rigid king-post structure comprising a beam 11 of box section and a vertical member 12 rigidly secured to the beam 11. A king pin or drive shaft 13 is rotatably mounted in aligned openings in the beam 11 and member 12 and as shown, bronze bearing bushes 14, 15, and 16 are provided at the upper and lower ends of the king pin 13. The upper and lower connecting members 10 of the tow arm 9 are secured to the drive shaft 13 by cotter bolts 17 and bronze bearing pads 18 and 19 are provided.

To the upper end of the drive shaft is rigidly secured, as by welding a lever arm 20 which engages in an anchor block 21 rigidly secured, as by welding, to the upper side of the tow arm 9. As the king pin 13 is positively connected to the tow arm 9, rotation of the king pin will produce a corresponding rotation of the tow arm to impart a turning movement to the trailer unit B to steer the vehicle.

The means for rotating the king pin 13 is best shown in Figures 14 and 15 and as shown a quadrant 22 is keyed to the lower end of the king pin 13 and at a position spaced forwardly thereof, a pair of links 23, 24 are pivoted, one link extending laterally of each side of the quadrant. The outer ends of the respective links are pivoted to swinging arms 25, 26 of L-like shape, the opposite ends of these arms having apertures through each of which extends a fulcrum pin 27 secured to the rigid beam 11 at a predetermined distance rearwardly of the king pin.

Intermediate their ends the arms 25, 26 are respectively connected by pivot pins 28, 29 to eyes 30, 31 connected with the piston rods 34 and 35 of hydraulically operated ram cylinders 32 and 33 of which are connected to fixed brackets 36 on the beam 11.

The four hydraulic cylinders 32/32 and 33/33 are connected together by two separate systems of hydraulic pipelines 37 and 38 in such a way that system 37 is connected to the forward ends of the off-side cylinders and the rearward ends of the nearside cylinders and system 38 is connected to the rearward ends of the offside cylinders and the forward ends of the nearside cylinders.

It will be seen therefore that when hydraulic pressure is applied in system 37 the offside cylinders will push out their piston rods and the nearside cylinders will pull in their piston rods, this combining to turn their connected swinging arms in one direction about the locus defined by the pin 27, and when pressure is applied in system 38 the opposite action throughout is effected. By this means the power of all four cylinders is harnessed—by way of the swinging arms 25 and 26, the links 23 and 24, and the Quadrant 22—to rotate the drive shaft 13 one way or the other.

The two pipe-line systems 37 and 38 are connected to the two separate output ports of a three-positional servo valve consisting of a valve body 39 and spring loaded valve plug 40. The other two ports of this valve are connected by a flow pipe 41 and a return pipe 42 to a high pressure hydraulic pump driven by the tractor engine.

In one position of this valve oil flows in from the pump by way of the flow pipe 41, through the valve body 39, and straight back to the pump by way of the return pipe 42. In this position of the valve the oil in the two pipe systems 37 and 38 remains locked in and the whole steering linkage remains locked in one position.

In the second position of this valve high pressure oil flows in from the pump by way of the flow pipe 41, through the valve body 39, and into pipe system 37, where it at once actuates the steering linkage. At the same time oil in the pipe system 38 is permitted to escape through the valve into the return pipe 42, whence it returns to the pump.

In the third position high pressure oil flows through the valve body into pipe system 38, this actuating the steering linkage in the opposite direction and allowing oil in system 37 to escape back to the pump.

The valve plug 40 is formed with a socket for a ball stud 43 formed on the lower end of pivot pin 28. At its forward end, the servo valve is connected by a drag link 44 to the normal steering box of the tractor which is operated by the tractor steering wheel 45.

Rotation of the steering wheel 45 in a clockwise direction by the driver results in the drag link 44 and the servo valve 39 40 being thrust powerfully rearwards against the ball stud 43 and this causes the internal mechanism in the valve body 39 to open the port which allows hydraulic pressure into system 37.

Conversely rotation of the steering wheel in an anti-clockwise direction results in the drag link and servo valve being pulled forwards against the ball stud and this causes the internal mechanism of the valve body to open the port which allows hydraulic pressure to flow into system 38.

By this means the tractor driver operates the steering wheel in a conventional fashion with normal effect but his every movement of the wheel is slavishly followed by hydraulic power harnessed to steer the vehicle in the manner described earlier.

In the event of failure of hydraulic power it will be seen that this arrangement allows for the manual effort applied at the steering wheel 45 to be transmitted to the drive shaft 13 by way of the drag link 44, the ball stud 43, the pivot pin 28, the swinging arm 25, the link 23 and the quadrant 22.

It will also be appreciated that hydraulic power may by this system be applied through one, two, three, or four of the hydraulic cylinders provided. Thus a damaged cylinder may readily be disconnected from the arrangement with a loss of only one-fourth of the total hydraulic effort provided.

It will also be understood that the required hydraulic power could be applied through a single large hydraulic

cylinder operating through a single swinging arm and a single link, but the provision of four small cylinders has many advantages over a single large cylinder or two medium cylinders.

As has been described already this steering arrangement results in a powerful torque being applied to the drive shaft 13, but this is secured by the lever 20 and the anchor block 21 to the tow arm 9 of the trailer and the result is that there is a reaction torque transmitted to the tractor unit. This causes the latter to swing to the right or to the left relative to the trailer unit and so the vehicle is steered.

The construction and arrangement of the link system in both embodiments is such that the rotational movement about the fulcrum pin 27 is magnified in being transmitted to the king pin 13 and by a suitable design of the various elements of the link system this magnification may be in the ratio of 2:1. This permits a turning movement of the tractor, trailer units in the order of 180° that is to say 90° each side of the normal fore and aft in-line position of the units which means that the vehicle has a manoeuvrability much greater than if the tractor unit A was fitted with normal steerable front wheels.

In rotating about the common fulcrum pin the angular relation between the swinging arms varies very slightly, but this variation is absorbed in the fluid connection between one side of the mechanism and the other, the movement referred to being very small.

The body 4 of the trailer unit is adapted to be tipped by operation of the tipping rams 46 or 51 which are adapted to rotate the body about the studs 8. It will be noted that as the body 4 is tipped the wheel-base of the vehicle is reduced as the axles of the tractor and trailer units are drawn nearer jack-knife fashion together. The construction of the vehicle is such as to permit this jack-knifing to happen whatever the articulated position of the units.

The brakes of the tractor and trailer are preferably independently operated and this enables a load to be dumped on a given spot by applying the trailer brake and allowing the tractor to be drawn rearwardly as the trailer body is tipped.

To facilitate travel over uneven ground, the tractor frame is mounted to permit a limited lateral movement. As shown more particularly in Figure 7 beam 11 has trunnion blocks 52, 47 respectively which are connected by pins 53, 48 to trunnion brackets 54, 49 welded or similarly secured to chassis cross members 55, 50. This arrangement permits relative movement of the beam 11 relative to the chassis approximately 20° each side of the vertical. The swing is limited by stops (not shown) welded to the cross members 55, 50.

It will be noted that should one of the rams become inoperative for any reason, the remaining ram or rams will be effective for imparting steering movements and even in the event of complete failure of the hydraulic system steering can still be effected through the mechanical connections between the steering wheel and king pin.

We claim :

1. Steering mechanism for effecting a turning movement of a trailer relative to a tractor, comprising a vertically disposed king pin rotatably mounted on the tractor and adapted to have a towing arm or the like of a trailer connected thereto, means for rotating the king pin comprising an arm mounted on the tractor for rotation about a locus spaced from the king pin along the longitudinal axis of the tractor, the arm extending laterally of the king pin and being connected thereto by a pivoted link, the arm and link being so arranged that a predetermined rotation of the arm about the said locus will effect a substantially greater rotational movement of the king pin to impart a steering movement.

2. Steering mechanism according to Claim 1 wherein the locus of the arm is disposed forwardly of the king pin, and the link is pivoted at one end to the said arm and at the other end to a member secured to the king pin and extending rearwardly thereof, such that the pivotal connection of the link to said member is spaced rearwardly of the king pin.

3. Steering mechanism according to Claim 1 wherein the locus point of said arm is disposed rearwardly of the king pin, and the link is pivoted at one end to said arm and at the other end to a member secured to the king pin and extending forwardly thereof, such that the pivotal connection of the link to said member is spaced forwardly of the king pin.

4. Steering mechanism according to Claim 2 or 3 wherein a pair of arms is provided each having one end rotatable about said locus and the opposite end extending laterally of one side of the king pin, a pair of links also being provided one end of each link being pivoted to the laterally extending end of one of the arms and the opposite end pivoted to the member connected to the king pin, the arms and links being symmetrically arranged such that one arm and its connected link are located on each side of the king pin.

5. Steering mechanism according to any one of the preceding claims wherein the said arm or arms is connected with a fluid pressure operated ram or rams operable to effect rotational movement of the arm or arms about said locus to impart a desired rotational steering movement to the king pin.

6. Steering mechanism according to Claim 4 wherein a separate fluid pressure operated ram is connected to each arm, valve means being provided for controlling the supply of fluid pressure to said rams such that in effecting a steering movement they are actuated in opposite directions to one another so that the arms are simultaneously rotated in the same direction about the locus.

7. Steering mechanism according to Claim 6 wherein the supply of fluid pressure for operating the rams connected with both arms is controlled by a common valve which is actuated by rotation of a conventional steering wheel of the tractor.

8. Steering mechanism according to Claim 6 wherein a separate valve is provided for controlling the supply of fluid pressure for each ram, one valve being adapted to be actuated by rotation of a conventional steering wheel on the tractor, and the other valve being interconnected with the first mentioned valve so as to be actuated simultaneously therewith but in an opposite sense.

9. Steering mechanism according to any one of the preceding claims wherein the king pin is rotatable in a sleeve to which the towing arm or the like is connected, means being provided for securing the sleeve to the king pin so as to be rotatable therewith.

10. Steering mechanism for effecting a turning movement of a trailer relative to a tractor substantially as described with reference to the drawings accompanying the Complete Specification.

11. Steering mechanism for effecting a turning movement of a trailer relative to a tractor substantially as described with reference to the accompanying drawings.

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OF DEPENNING & DEPENNING.

Agents for the Applicants.

Dated this 29th day of December 1960.

MGIP Santh.—SL—34 Patent/62—11-2-63—100.

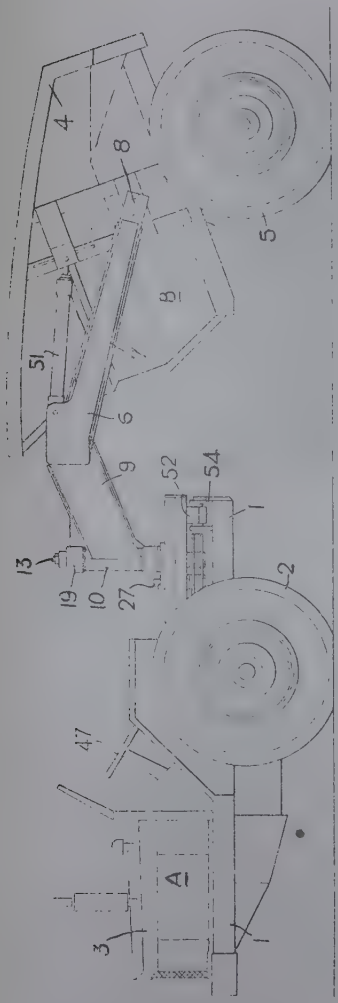

FIG. 1.

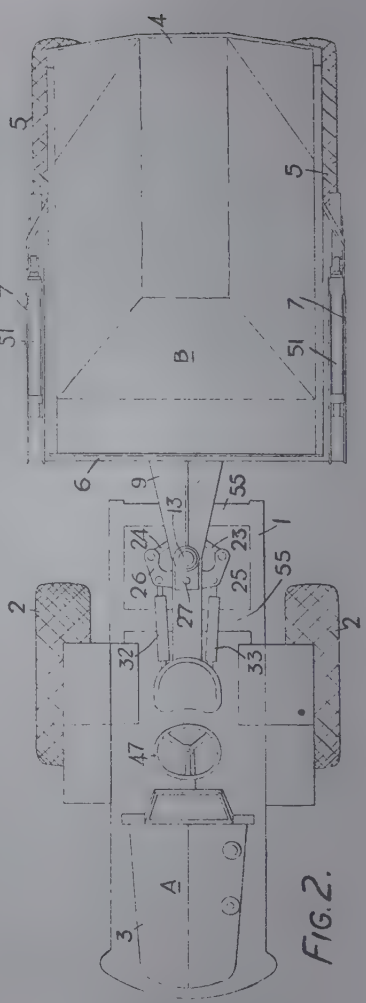

FIG. 2.

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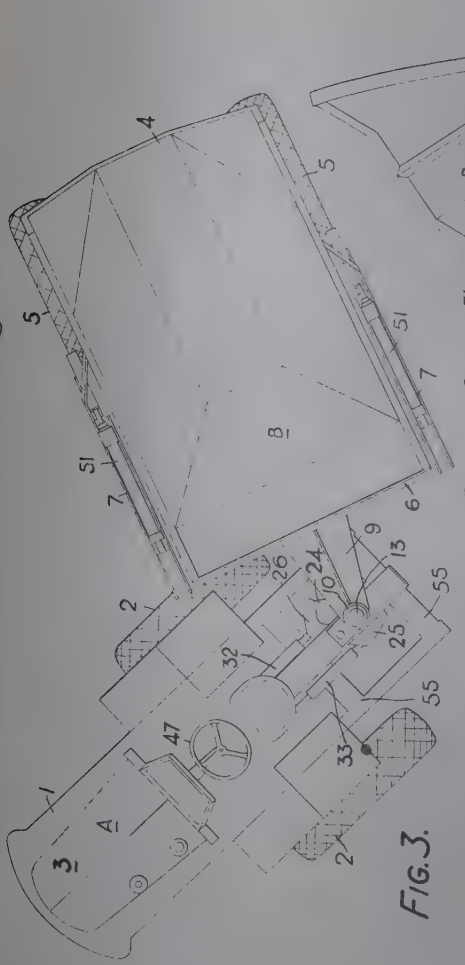

FIG. 3.

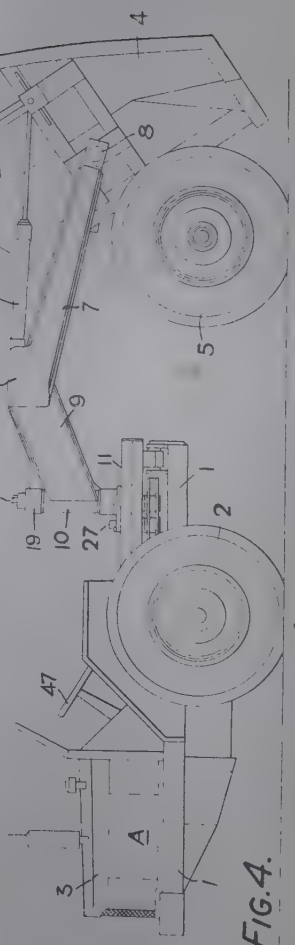

FIG. 4.

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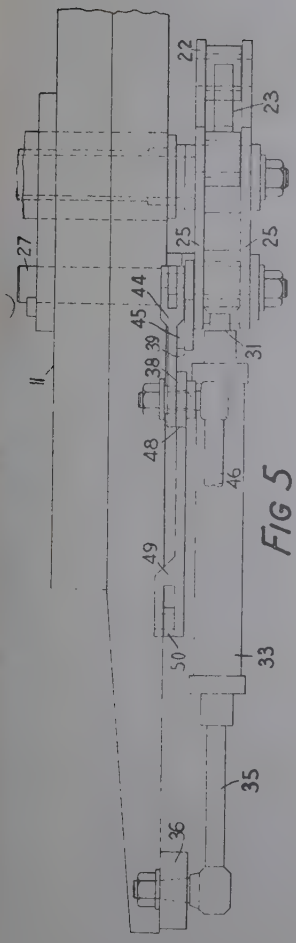

FIG 5

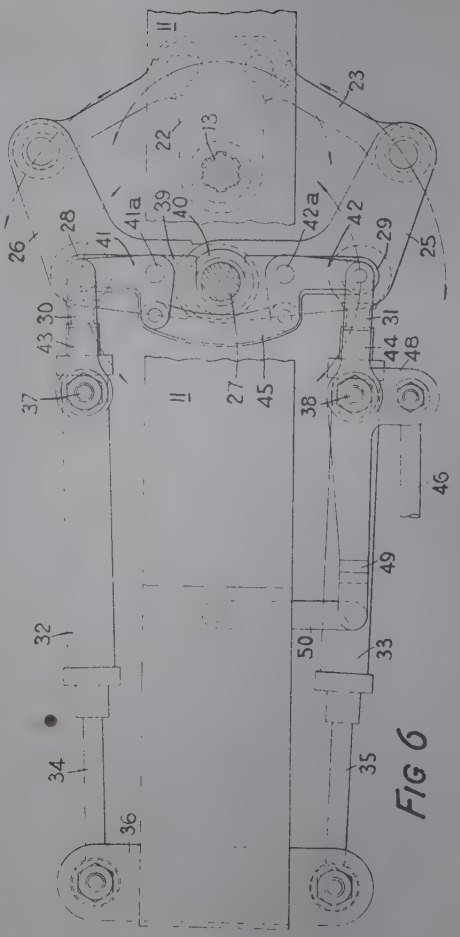

FIG 6

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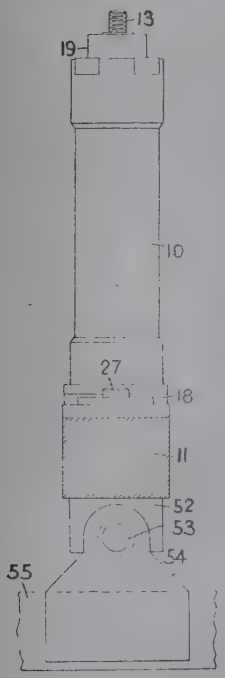

FIG. 8.

FIG. 9.

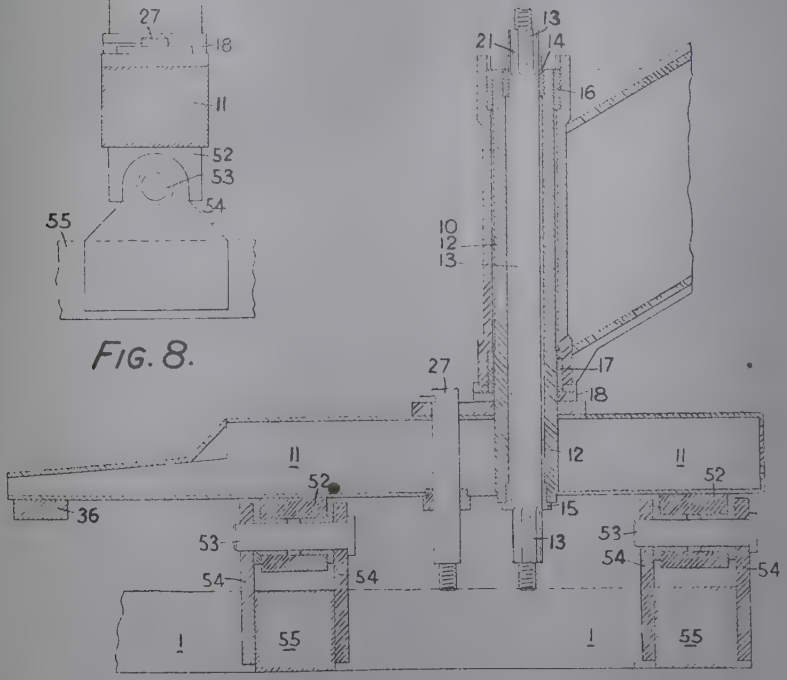

FIG. 7.

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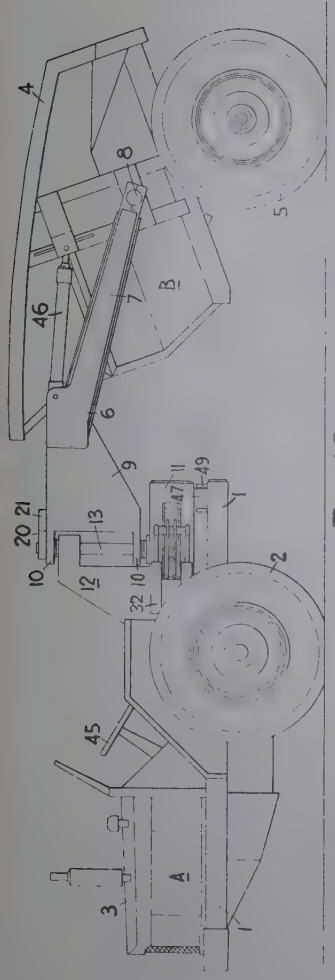

FIG. 10.

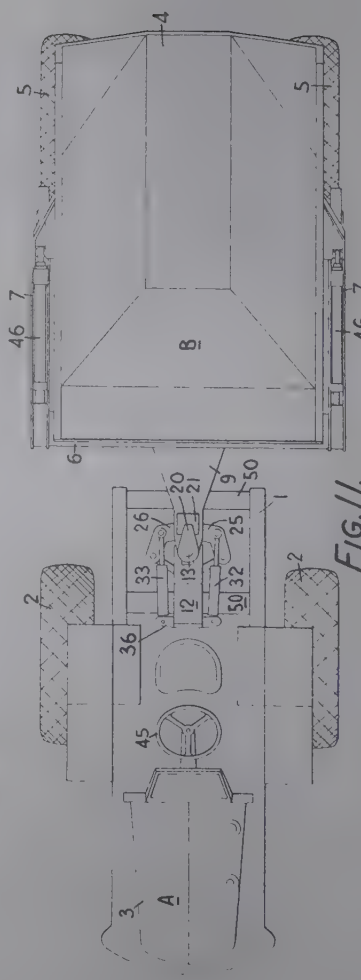

FIG. 11.

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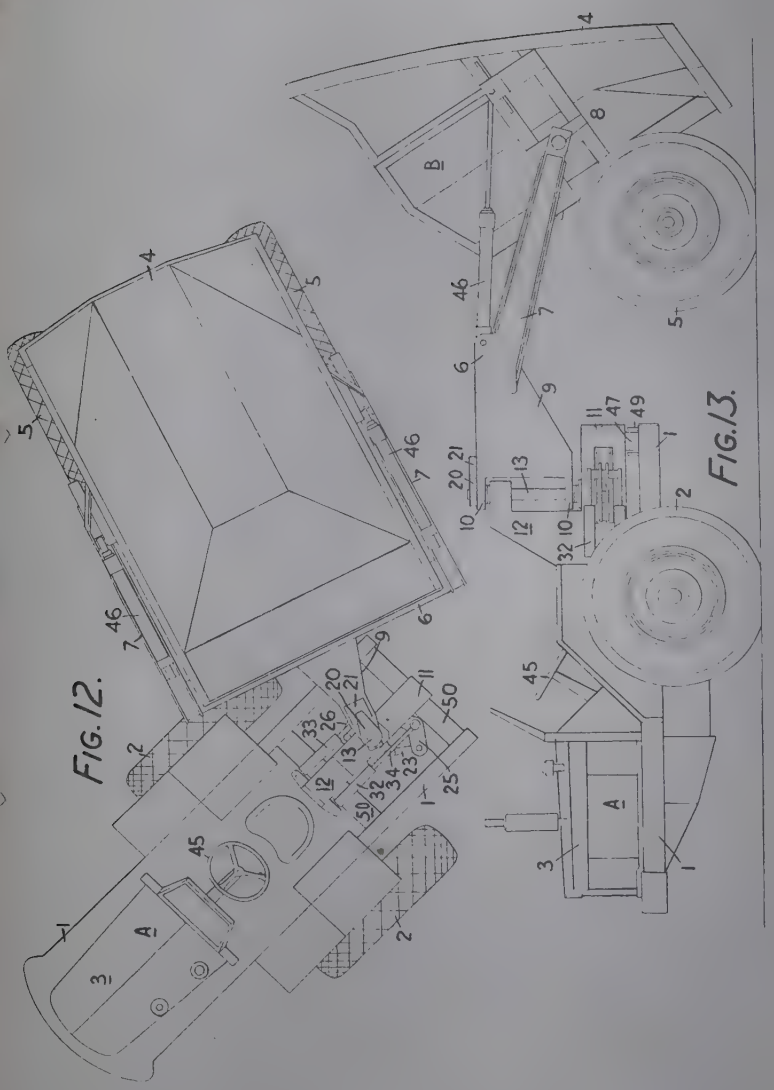

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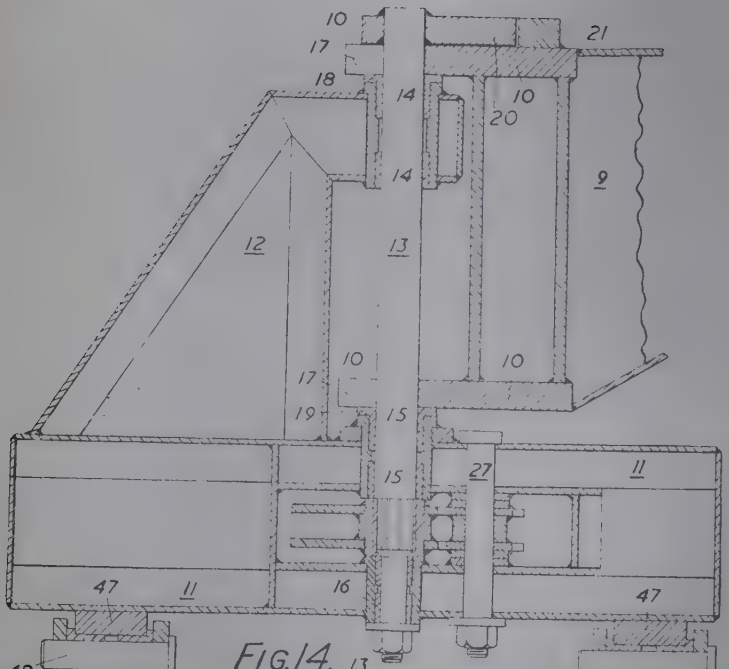

FIG. 14.

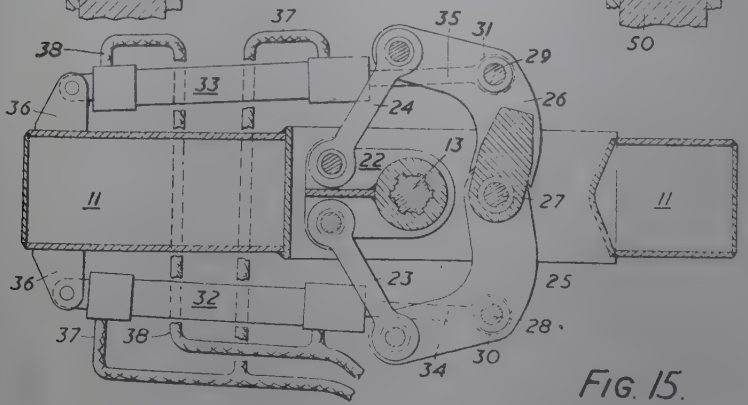

FIG. 15.

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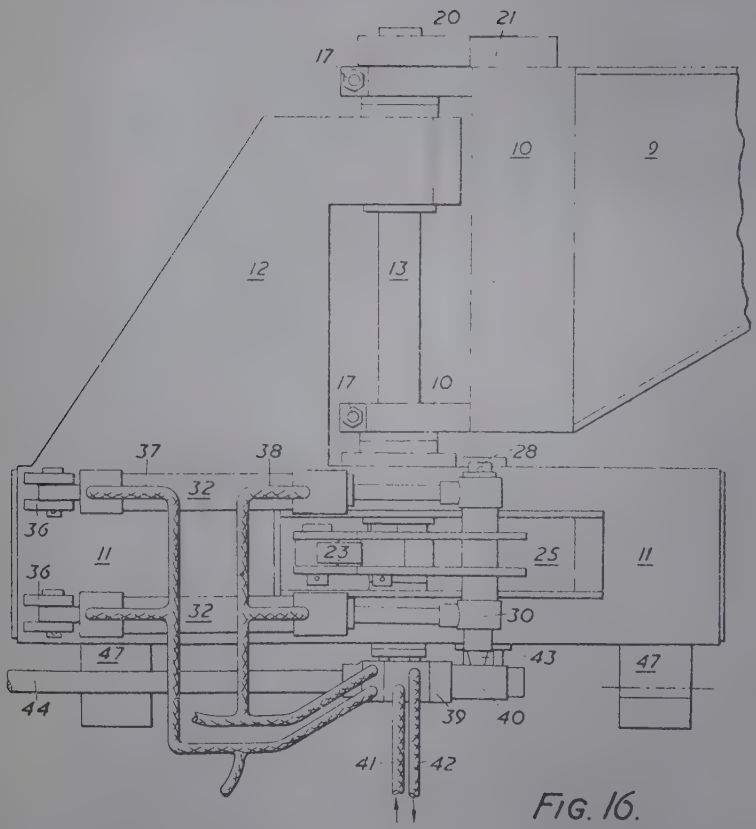

FIG. 16.

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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74734, filed 29th December 1960./8 Paus, 1882 (Saka).

Accepted 6th June 1962.

"RESILIENT MOUNT FOR LOAD-CARRYING ANTI-FRICTION BEARINGS"

LUDWIG BINDER & CO. A Firm duly organised under the Laws of Austria, of Alte Poststrasse 98, Graz-Eggenberg, Austria.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

The present inventin provides a resilient mount for anti-friction bearings. In this connection the term mount refers to means which provide such a support for the anti-friction bearing that the outer race of the anti-friction bearing is connected by an annular member of resilient material to the frame or other machine part which carries the bearing rather than to a support carried by a practically non-yielding machine part, as is the case in most instances at the present time. Such a resilient mount can increase the load capacity of the bearing because it provides for a more uniform distribution of the load. According to the invention the resiliently deformable intermediate member disposed between the outer race of the anti-friction bearing and the machine part carrying this bearing has a special shape and is pre-stressed to provide for special additional results, as will be set forth hereinafter.

Resilient intermediate members which are inserted between the anti-friction bearing and its support are known but according to the prior art are inserted only under a small initial stress, as can be achieved during assembly. Owing to the low pressure by unit area in the bearing mount such assemblies cannot transmit the load which corresponds to the load capacity of the rigidly fitted bearing and for this reason they cannot increase the load capacity of bearings of this type. Only a resilient support is actually achieved so that the usefulness of such assemblies is restricted to special cases,where movements of the bearing under the influence of the load are tolerable.

In connection with pulleys for conveyor belts it has already been proposed to provide between the outer race of the load-carrying anti-friction bearing and the periphery of the pulley a resilient intermediate member, which is under axial intial compressive stress. In this cash, however, no care is taken to have the outer race of the anti-friction bearing directly engage the resilient intermediate member but the outer race engages a pair of shells, which are axially forced together to deform the resilient ring, which is spaced from the outer race of the anti-friction bearing, so that this ring is clamped between said shells and the inside periphery of the carrying roller. Since these shells bear directly on the outer race of the anti-friction bearing and support the same, they form a more or less rigid support for this race. The load resistance of an anti-friction bearing can only be increased, however, if an adequate load capacity of the outer support of the anti-friction bearing is retained and nevertheless the outer race of the anti-friction bearing is rendered yieldable to some extent in the direction of the bearing load, i. e., transversely to the axis of the bearing. This will only be the case if a resilient support of the outer race of the anti-friction bearing is provided for.

Such a deformation of the outer race has the practical result that more rolling elements can be used for transmitting the bearing load from the shaft carried by the bearing to the frame machine or another element of construction which takes up the pressure than where such deformation does not take place. It may be imagined that the outer race hugs, as it were, the envelope of the rolling elements. Thus, the combination of a resilient member directly engaging the outer race of the anti-friction bearing with the possibility of maintaining the same under sufficient axial pressure results in a substantial increase in the load capacity of the bearing in addition to the mere shock absorption provided by the known resilient design.

Having regard to these matters, the invention proposes a resilient element which is deformed by pressure in an axial direction resulting from the use of tie-bolts and thereby wedges itself in a radial direction, the resilient element, preferably of disc form, laying directly against the outer race and preferably extending to the inner face of the machine part supporting the bearing.

The present invention includes further other developments of these basic ideas based upon ths following considerations :

The tie bolts required in anti-friction bearing assemblies of the kind under discussion here acts on the resilient intermediate members by means of thrust members, which are in most cases ring-shaped.

Due to the friction between the engaging surfces of the pre-stressing members and the resilient intermediate members, pressure will always build up over the outer race of the anti-friction bearing and will tend to deform the resilient intermediate members in the shape of a barrel. There will necessarily be a stress variation over the outer race of the anti-friction bearing. The maximum will always occur at the center of the outer race and the stress will decrease to zero towards the rim. Besides the fact that this involves an undesirable loading of the resilient intermediate member and the pre-stressing means, the initial stress will cause a deformation of the outer race of the ball bearing itself. This is subjected to the greatest initial stress in that region where it has the smallest cross-sectional area owing to the provision of the bearing groove whereas in the rim zones, where the ring has a large thickness, the initial stress approches zero. This gives rise to transverse bending stresses in the outer race of the anti-friction bearing and the cross-sectional shape of the outer race does not remain flat. Particularly in self-aligning ball and roller bearings this results in a substantial disturbance of the running characteristics and the load is no longer equally distributed to both runways.

The actual useful load on the bearing will then impose an additional load on the bearing mount with approximately the same pressure distribution so that the abovementioned deterioration of the accuracy of running will be intensified.

To minimize this undesired additional transverse deformation of the outer race and thus to ensure that the running characteristics of the anti-friction bearing operating under increased load will be adversely affected to the least degree, the invention teaches to provide an intermediate member, which is deformed, as is known per se, by being compressed in the axial direction by means of tie bolts and co-acts directly with the outer race of the anti-friction bearing, and which has such a profile and/or consists of such a material that when axially compressed it will exert on the outer race of the anti-friction bearing a pressure which when coinsidered in an axial sectional view over the outer boundary of this outer race. exhibits such a non-linear variation that pressure maxima occur adjacent to the end faces of the outer race and a pressure minimum occurs

in the intermediate portion of this race In consideration of the cross-sectional shape of the outer race of the ball bearing this will ensure that the same will be subjected to a uniform compressive stress so that transversebending will be avoided.

The diagrammatic drawings show illustrative embodiments of the invention. Fig. 1 and the corresponding side view shown in Fig. 2 as sectional view taken on line II-II of Fig. 1 as well as Figs. 3 and 4 provide a general explanation of the basic idea of the invention. Figs. 5-8 show various possibilities of carrying out the invention, in views substantially restricted to the resilient intermediate members, which are shown in section. Figs. 9-11 serve to illustrate a further development of the invention.

Figs. 1 and 2 shows an anti-friction bearing which consists of the inner race 1, the outer race 2 and the rolling elements 3 and together with a resilient intermediate member 6 connects the shaft 4 to the part 5 which carries the bearing. The resilient intermediate member 6 is axially compressed by means of tie bolts 7, which extend through the holes 6a and which act on the intermediate member 6 by means of thrust rings 8.

With reference to Fig. 1 it may be assumed first that parts. 1, 2, 3 are rigid and the intermediate member 6 is rigid too. The ball 3a will then have to transmit substantially the entire load which is assumed to act vertically on the bearing. The conditions are practically improved in that the ball 3a is resiliently flattened to some extent under the load and is slightly forced into the race so that the adjacent balls are also slightly deformed and participate in transmitting the load on the bearing. The resulting distribution of the effective useful load is unsatisfactory. It might be substantially increased if part 6 consists of resilient material so that it permits of a substantially elliptical deformation of the outer race 2 and the same engage a large number of rolling elements with almost the same force without causing the latter to become impressed into the bearing groove of the outer race ; this will substantially increase the load capacity of the bearing. Features of this character form the basic subject matter of this patent.

Whereas the abovementioned features permit of a substantial increase in the load capacity of the anti-friction bearing, they do not permit of utilizing further possibilities, inherent in design, of increasing the bearing load and it has been found that the following facts are decisive for this restriction.

The distribution of pressure under the useful load of the bearing is similar to the distribution of pressure under the axial prestressing force. Fig. 3 shows this distribution of pressure for an intermediate member 6 which has a rectangular cross-section and which is under the intial axail stress P imposed by means of the prestressing ring 8. Under the initial axial stress the cross-section of the ring 6 is deformed like a barrel so that a load line q is built up over the outer race 2 of the bearing. As a result the race 2 bends in the transverse direction approximately in accordance with the resilient line y. This transverse curvature of the bearing ring deteriorates the running characteristics of the anti-friction bearing.

Fig. 4 shows the resilient intermediate ring 6 which is profiled according to the invention and which when subjected to an intial stress P builds up a load lind q_1, which is more in accordance with the cross-sectional shape of the outer race so that it does not cause a distributing transverse deformation theteof. The resilient line y_1 is then approximately straight.

Because the useful load on the bearing is mainly taken up by arch action by means of the ring if resilient mounts are employed, the same remarks as have been set forth hereinbefore regarding the transverse bending of the outer race of the ball bearing and the resulting influence on the running characteristics of the anti-friction bearing apply also to this useful load on the bearing. A further result of the pressure distribution according to Fig. 3 resides in that the system comprising the intermediate member 6 and the race 2 is in a state of unstable equilibrium because deformation energy is released during each tilting movement as only unloaded rim zones of the resilient intermediate member are subjected to higher pressure whereas the highly loaded intermediate zone is relived from stress. Where the pressure is distributed according to Fig. 4, this difficulty is avoided owing to higher pressures acting in the outer zones. Due to these difficulties the load capacity of the anti-friction bearing cannot be utilized more fully in accordance with the above mentioned prior proposals. Thus, the present invention resides substantially in that a resilient bearing mount is inserted between the machine part and the outer race of the anti-friction bearing and this mount is so shaped that when it is subjected to the required initial stress the pressure distribution over the axial extent of the outer race is such that increased pressure occur in the rim zones whereas the inner zone remains under a smaller load. For this purpose, the resilient intermediate member 10 shown in cross-section in Fig. 3 has a profile which when subjected to pressure in the direction of the arrows P applies to the outer race 2 a load which follows approximately the line q_1. In addition to the increase in the safe load on the bearing which is now possible, the incorporation of the ball bearing into the resilient bearing mount according to the invention permits of a compensation of all dimensional tolerances so that the difficulties are overcome which are involved in the manufacture of the ball bearing seats. It is quite in accordance with the invention that in this case the bore in the machine element 5, Figs. 1 and 2, and the outer race 2 of the anti-friction bearing, are not subjected to further machining which results in a reduction in cost.

The bearing mount according to the invention is further capable of protecting the anti-friction bearing from impact to the highest possible degree. Furthermore, vibration in a radial direction is prevented by the high initial stress imposed on the bearing. On the other hand, a movement of the bearing in an axial direction, as may be required, e. g., for taking up thermal expansion, is quite possible independently of the high initial stress because this is substantially determined only by the shearing strength of the transition zone between the mount and the machine part.

The increased compressive stressess in the rim zone ensure that the bearing will resist tilting.

To prevent a relief of stresses in the angular range between the stressing ring and the outer race of the anti-friction bearing, the resilient mount may be partly drawn inwardly over the outer race and is subjected to substantial pressure in an axial direction by the stressing device, which is also radially inwardly extended. This pressure acts between the lateral boundary of the outer race and the tightening disc.

Fig. 5 shows another resilient intermediate member 11 according to the invention. This intermediate member has a rectangular profile when it is not loaded and contains two sheet metal inserts 12 spaced from the end faces 11a and from the symmetry plane extenting at right angles to the axis of the intermediate member. The sheet metal inserts may be integral with the rubber member 11. A third insert 13 of this kind is disposed in said plane of symmetry. Since the distances between these inserts differ, a load exerted by forces P will result in a distribution of forcess according to line b, with minimum values in the planes of the inserts 12, 13. The intermediate member has inside flange-like extensions 14a overlaping the outer race of the anti-friction bearing.

The resilient annular member 14 of Fig 6 comprises elongation-resisting inserts 15, suitably of metal, the profile of which provides thrust faces 15a, which cause the rim portions of the intermediate member 15 to yield more than the inner part toward the outer race of the anti-friction bearing when the inter-

mediate member is subjected to pressure P in the axial direction of the anti-friction bearing.

It may be suitable in accordance with the basic concept of the invention to provide an intermediate member which behaves like a non-homogeneous resilient member when considered in the radial direction so that there is a variation in its axial compressive stress considered over its radial extent and in its resilient characteristics. To achieve this thrust members 16 might be used which are urged against the intermediate member 14 with profiled end faces 16a, as shown in Fig. 6, rather than with plane end faces.

Fig. 7 shows a mount according to the invention in which the thrust rings 18 form bearing covers. Fig. 8 shows a modification of this idea inasmuch as the resilient members are not passed through by tie bolts but a thrust ring 19 forming a bearing cover is threaded to an extension 20a of the carrying part 2a and acts on the resilient intermediate member 21 by an extension 19a. The same applies to the second thrust ring.

A further improvement of the anti-friction bearing mount according to the invention will be obtained if the resilient intermediate members compressed in the axial direction behave like non-homogeneous resilient members at least in a radial direction so that there is a variation in their axial compressive stress, considered over the radial extent of these transmitting members, as well as in the resilient characteristics thereof. For a more detailed explanation of this aspect of the invention, reference is made to Figs. 9-11 Figs. 10 and 11 are sectional views showing details of intermediate members of the last-mentioned kind and of their thrust parts.

According to Fig. 9 the ball bearing having an outer race 5 shown in elevation is fitted on a shaft 4 and connected by a rubber ring 24 to the fixed carring part 25. For this purpose, the ring 5 is axially comprrssed by tie bolts 7 and thrust rings 26 with the result that it exerts pressure in the direction a, b on the parts 5 and 25, which are bridged by the ring 5.

According to the previously accepted theory, such a rubber member subjected to the compressive stress illustrated will be similar in behaviour to a liquid, i. e., the pressure exerted by the annular member on the surfaces engaged thereby should be approximately equal at all points. As has been set forth hereinbefore in conjuction with Figs. 3 and 4, this assumption is not correct. Whereas a and b may be considered equal if the cross-section is rectangular and the thrust ring 26 are contrary disposed, this is not due to the symmetrical arrangement chosen rather than because a rubber member subjected to pressure would behave like a liquid, which it does not. On the other hand, the equality of a and b, Fig. 9, is not an advantage. On the country, the substantial difference between the areas of the two surfaces engaged by the rubber ring on the inside and outside and difference between the fits or pressures required on the inside and outside would require a much larger pressure per unit area on the inner race. Furthermore : If it is desired that the shaft 4 should retain a certain freedom of axial movement relative to the bearing mount, the ring must be still sufficiently movable in the axial direction in some region and since the pressure per unit of area under which the intermediate member 24 engages the part 25 may be less than between the intermediate member 24 and the anti-friction bearing, this freedom of movement should suitably exsit in the range between the periphery of the thrust ring 26 and the carrying part 25. It will be apparent from the above that a rubber member which actually behaved like a liquid body when subjected to pressure would be a failure in every respect. Although this assumption regarding behaviour is not confirmed in practice, the actual behaviour is by no means satifactory and will give satisfactory results only in very rare, exteremely simple cases. On the other hand, it will be appreciated that more favourable conditions will be obtained in accordance with the invention if the member 24 behaves like a non-homogeneous resilient member also in the radial direction. For instance, if an elongation resisting itsert such as of linnen or wire, was embeded in the member 3 and 27, this insert will obviusly result in a reduction of the pressure exerted by the member 24 on the carrying part 25. At the same time such an insert would have the result that that portion of the member 24 which is disposed outside the insert 27 remains softer. This is of advantage for the performance of the abovementioned axial movement.

Similar effects can be achieved with a simpler structure if according to a feature of the invention at least one thrust ring 26 is so designed that its end face acting on the resilient intermediate member has a curved generatrix and this carvature causes the ring 26 when compressed to exert pressure on the rubber member 24 in such a manner that there is a variation in its pressure distribution and resilient characteristics, considered over its radial extent. It is thus possible with simple means to ensure over this radial extent any distribution of pressure which may be required for the bearing in any specific case. This may be achieved merely by giving the thrust ring an appropriate profile. It is also possible within the scope of the invention to adopt additional measures which promote this aim, such as the profiling of the intermediate member described hereinbefore, the use of elongation-resisting inserts etc.

Fig. 10 shows the inside surface 30 and the outside surface 31 corresponding to members 5 and 25 of Fig. 9, the intermediate member 32 and the thrust rings 33, the thrust bolts of which are not shown but should be imagined to act through the holes 33a. The thrust rings 33 have a non-rectangular cross-section and are formed on the inside and outside with a protruding ridge or bead 33b, which causes the intermediate member 32 to be deformed mainly in the outer or peripheral ranges. A ring 33 penetrating into the intermediate member 32 deforms the former approximately according to line 34 while forming peripheral zones of increased pressure whereas the central part of the intermediate member 32 is under smaller axial pressure.

In the illustrative embodiment shown in Fig. 11 the rubber ring 36 has a slight outward taper. The rings 37 terminate at a larger distance from part 31. This results in a strong pressure being exerted on the intermediate member 36 close to part 30, which is assumed to correspond to the crrrying part 25 of Fig. 9 and a low pressure being exerted close to the part 31, and the formation of a fairly large zone 39 of lower pressure so that this bearing assembly is capable of yielding substantially both in the axial and radial directions.

WE CLAIM :--

1. A resilient mount for load-carring anti-friction bearings having a resilient intermediate member, which is disposed between the outer race of the bearing and the part which receives the bearing, which intermediate member exerts pressure in inward and outward radial directions, charcterized in that the intermediate member is deformed in a manner known per se by being subjected to pressure in the axial direction by tie bolts and co-acts directly with the outer race of the anti-friction bearing.

2. Mount according to Claim 1, characterized in that the intermediate member has such a profile and/or consists of such a material that when axially compressed it will exert on the outer race of the anti-friction bearing a pressure which when considered in an axial sectional view over the outer boundary of this outer race exhibits such a non-liner variation the pressure maxima occur close to the ends of the outer race and a pressure minimum occurs in the intermediate portion of this ring.

3. A resilient mount according to Claim 1 and 2, characterized in that the intermediate member, which is annular, as is known per se, consists of a uniform resilient material and that boundary face of the intermediate member which co-acts with the outer race of the anti-friction bearing has a cross-section having a concave boundry.

4. A resilient mount according to Claim 1 and 2, characterized in that the intermediate member which consists of resilient material and is annular, as is known per se, has at least two inserts of inelastic material, suitably in the form of annular sheet metal discs, which are spaced from the end faces and from the vertical plane of symmetry which is at right angles to the axis of the intermediate member.

5. A resilient mount according to Claim 1 and 2, characterized in that the annular intermediate member has elongation-resisting inserts 15, suitably of metal, the profile of which has thrust faces 15a, which cause the rim portions of the intermediate member to yield more toward the outer race of the anti-friction bearing than the inner portion of the intermediate member when the intermediate member 15 is subjected to pressure P in the axial direction of the anti-friction bearing.

6. A resilient mount according to Claim 1, characterized in that the annular intermdiate member, which is annular in a manner known per se, has inside flange-like extensions overlapping the outer race of the anti-friction bearing.

7. A resilient mount according to any of Claims 1 to 6, characterized in that the intermediate member behaves like a non-homogeneous resilient member in a radial direction so that there is a variation in its axial compressive stress, considered over its radial extent, and in its resilient characteristics.

8. A resilient mount according to Claim 7, characterized in that the end face of the intermediate member and/or of the thrust members axially compressing the same have a generatrix which is so curved that the pressure exerted by the rings varies over their radial extent.

9. A resilient mount according to any of Claims 1 to 8, characterized in that the tie bolts act in known manner by means of thrust rings on the intermediate member and that this thrust ring forms a bearing cover.

10. A resilient mount according to any of Claims 1 to 9, characterized in that the tightened thrust rings engage an extension of the support for the bearing to determine the highest possible initial stress of the intermediate member.

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Agent for the Applicants.

Dated this 29th day of December 1960.

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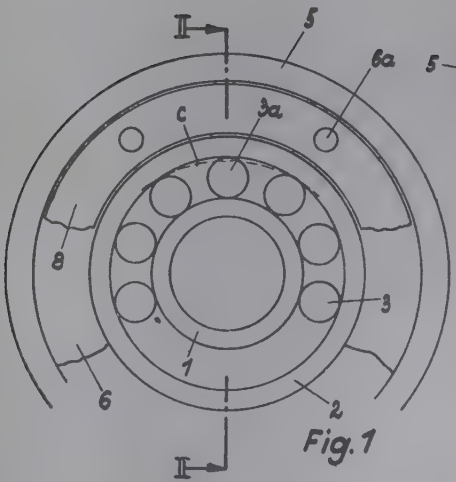

Fig. 1

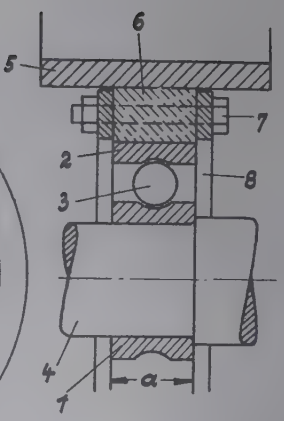

Fig. 2

Fig. 3

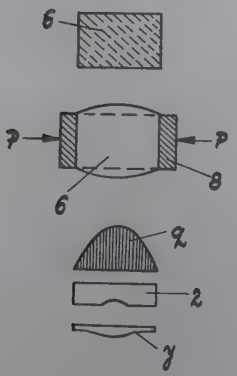

Fig. 4

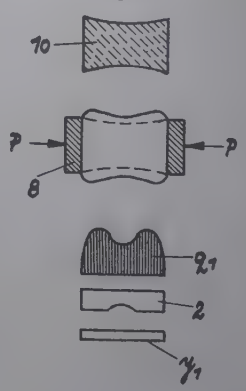

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Fig.5

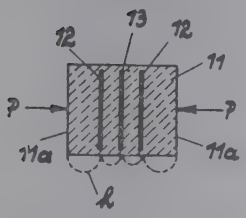
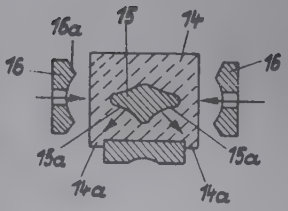


Fig.6



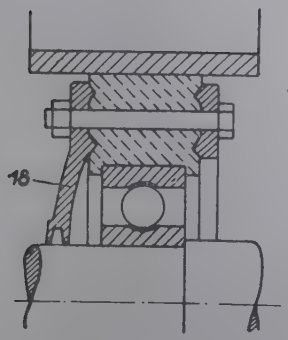


Fig.7

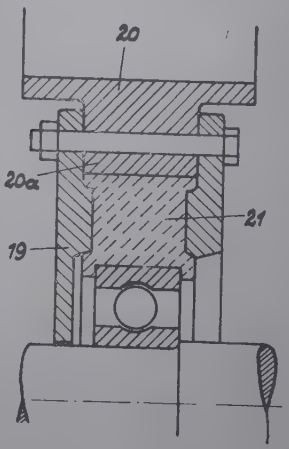


Fig.8

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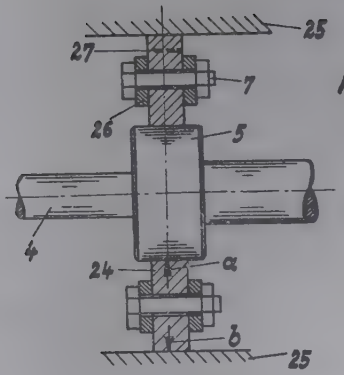

Fig. 9

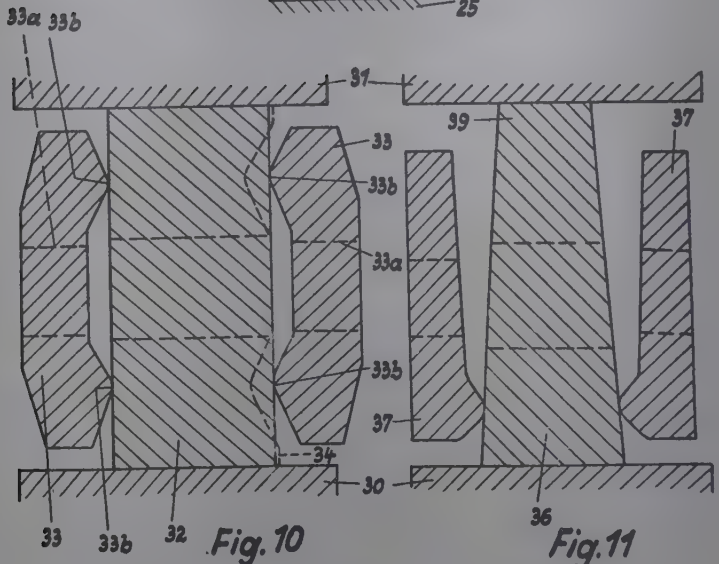

Fig. 10

Fig. 11

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GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 74735. Application No. 74735, dated 29th December 1960. (Divided out of No. 69382) [Application and Provisional Specification antidated to 19th October 1959 under section 5 of the I. P. & D.—Act 1911.] Complete Specification left on 29th December 1960. [Complete Specification antidated to 8th August 1960, under Section 5 of the I. P. & D.—Act 1911.] (Application accepted 12th July 1961.)

ANIMAL FEEDING STUFFS CONTAINING NEW 18-0-METHYL RESERPIC ACID METHYL ESTER.

PROVISIONAL SPECIFICATION

CIBA LIMITED, Chemical Manufacturers, a Swiss Corporation, of 141, Klybeckstrasse, Basle, Switzerland.

The following specification describes the nature of this invention.

The present invention concerns ethers of deserpidates. More particularly, it relates to 18-0-ethers of deserpidates having the formula shown in Fig. 1 of the accompanying drawings, in which R_1 represents lower alkyl, lower alkoxy-lower alkyl or tertiary amino-lower alkyl, R_2 stands for lower alkyl, R_3 represents a lower aliphatic hydrocarbon or a substituted lower aliphatic hydrocarbon radical, R_4 stands for hydrogen, lower alkyl, lower alkoxy, monocyclic carbocyclic aryl-lower alkoxy, lower alkyl-mercapto or halogen, each of the substituents R_5, R_6 and R_7 represents primarily hydrogen, or one of the substituents characteristic of R_4, whereby two neighbouring substituents, when taken together, may also form a lower alkylenedioxy radical, and each of the radicals R_8' and R_8'', represents hydrogen or lower alkyl, and salts thereof, and process for the preparation of such compounds.

A lower alkyl group R_1 stands, for example, for methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, isopentyl, n-hexyl and the like.

In a lower alkoxy-lower group R_1, the lower alkoxy portion may be, for example, methoxy, ethoxy, n-propyloxy, isopropyloxy and the like. The tertiary amino group of a tertiary amino-lower alkyl radical R_1 is primarily an N,N-di-lower alkyl amino group, in which lower alkyl contains from one to four carbon atoms, *e.g.*, dimethylamino, diethylamino, di-n-propylamino or diisopropylamino and the like, an N,N-lower alkylene-imino group, in which lower alkylene contains from four to six carbon atoms, *e.g.*, pyrrolidino, piperidino or hexamethyleneimino, an N,N-lower oxa-alkylene-imino group, in which lower oxa-alkylene contains, preferably, four carbon atoms, *e.g.*, morpholino, or an N,N-lower aza-alkylene-imino group, in which lower aza-alkylene contains, preferably, four carbon atoms, *e.g.*, N-methyl-piperazino.

The lower alkyl portion of a lower alkoxy-lower alkyl radical R_1 or a tertiary amino-lower alkyl radical R_1 is represented by a lower alkylene radical, which separates the lower alkoxy group or the tertiary amino group from the carbonyl portion of the carboxyl group by at least two, preferably by two to three, carbon atoms. Such radicals are primarily 1,2-ethylene, 1-methyl-1,2-ethylene or 2-methyl-1,2-ethylene or 1,3-propylene; other lower alkylene radicals may be 1,4-butylene or 1-methyl-1,3-propylene and the like.

The lower alkyl group R_2 may stand for ethyl, propyl, isopropyl, but represents above all methyl.

Generally, R_3 represents a lower aliphatic hydrocarbon or a substituted lower aliphatic hydrocarbon radical; substituted lower aliphatic hydrocarbon radicals may contain as functional groups lower alkoxy, tertiary amino and the like R_3 represents, primarily, lower alkyl, such as, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, isopentyl or n-hexyl and the like. These radicals may contain as functional groups lower alkoxy, *e.g.*, methoxy or ethoxy and the like, tertiary amino-lower alkyl, such as N,N-di-lower alkyl-amino, *e.g.*, N,N-dimethylamino, N-ethyl-N-methyl-amino, N,N-diethylamino and the like, N,N-lower alkylene-imino, in which alkylene contains, primarily, from four to six carbon atoms, *e.g.*, pyrrolidino, piperidino, hexamethyleneimino and the like, N,N-lower oxaalkylene-imino, in which alkylene contains, primarily, four carbon atoms, *e.g.*, morpholino, N,N-lower aza-alkylene-imino, in which alkylene contains, primarily, four carbon atoms, *e.g.*, 4-methyl-piperazino and the like. Preferably, these substituents are separated from the oxygen atom of the 18-position of the deserpidate nucleus by at least two, advantageously, by two to three, carbon atoms. Substituted lower aliphatic hydrocarbon radicals, representing R_3, are, therefore, 2-lower alkoxy-ethyl, *e.g.*, 2-methoxyethyl or 2-ethoxyethyl, 3-lower alkoxy-propyl, *e.g.*, 3-methoxypropyl, 2-N,N-di-lower alkyl-amino-ethyl, *e.g.*, 2-dimethylaminoethyl or 2-diethylaminoethyl, 3-N,N-di-lower alkyl-aminopropyl, *e.g.*, 3-dimethylamino-propyl, or 2-N,N-lower alkylene-imino-ethyl, *e.g.*, 2-(1-piperidino)-ethyl, or 3-N,N lower alkylene-imino-propyl, *e.g.*, 3-(1-pyrrolidino)-propyl, and the like.

The substituent R_4 represents primarily hydrogen or lower alkoxy, *e.g.*, ethoxy, n-propyloxy, isopropyloxy, or particularly methoxy. It may also stand for monocyclic carbocyclic aryl-lower alkoxy, *e.g.*, benzyloxy, lower alkylmercapto, *e.g.*, methyl-mercapto or ethylmercapto, lower alkyl, *e.g.*, methyl or ethyl, or halogen, *e.g.*, fluorine, chlorine or bromine. The substituents R_5, R_6 and R_7 represent primarily hydrogen; they may also stand for the substituents characteristic for R_4, such as, for example, lower alkyl, *e.g.*, methyl or ethyl, lower alkoxy, *e.g.*, methoxy or ethoxy, or halogen, *e.g.*, chlorine or bromine. Furthermore, two neighbouring substituents selected from R_4, R_5, R_6 and R_7, when taken together, may form a lower alkylenedioxy, *e.g.*, methylenedioxy, radical.

Each of the radicals R_8' and R_8'', stands preferably, for hydrogen; when representing lower alkyl, such radical may stand for ethyl, or primarily for methyl

Salts of the new compounds of this invention are pharmaceutically acceptable addition salts with acids, primarily with inorganic acids, such as mineral acids, *e.g.*, hydrochloric, hydrobromic, sulfuric or phosphoric acid and the like, or with strong, organic acids, *e.g.*, acetic, hydroxyacetic or methane sulfonic acid and the like.

The new compounds of this invention have sedative and tranquilizing effects on the central nervous system; they may also exhibit antihypertensive properties. Furthermore, tests show that animals, treated with the compounds of the present invention, recover faster and more completely from the pharmacological effects than those treated with known, naturally occurring Rauwolfia alkaloids, such as reserpine, deserpidine or rescinnamine. In addition, certain quantitative differentiations may be observed within the group of the new compounds of this invention. Thus, when compared with the established ratio existing between antihypertensive and sedative effects in the above-mentioned natural Rauwolfia alkaloids, some of the compounds of this invention have more predominant sedative effects with negligible antihypertensive activity, where as in others, the latter effect may be more pronounced than the sedative and tranquilizing component.

The compounds of the present invention may, primarily, be used as sedative agents to relieve states of hyperactivity, tension and agitation as, for example, associated with mental disturbances. Compounds with a predominating antihypertensive effect may also be employed as antihypertensive agents to relieve hypertensive conditions as, for example, benign or malignant hypertension, renal hypertension or hypertension associated with pregnancy, such as toxemia of pregnancy.

The above-described properties are particularly exhibited by lower alkyl, 2-lower alkoxy-ethyl or 2-N,N-di-lower-alkyl-amino-ethyl 11-R_4-18-0-R_3-deserpidates, in which R_6 stands for lower alkyl, especially methyl, and R_4 for hydrogen or methoxy. Representing this group of compounds are lower alkyl, *e.g.*, methyl, ethyl, n-propyl or n-butyl, 18-0-methyl-deserpidate or lower alkyl, *e.g.*, methyl, ethyl, n-propyl or n-butyl, 18-0-methyl-reserpate, lower alkoxy-lower alkyl, *e.g.*, 2-methoxyethyl, 18-0-methyl-deserpidate, lower alkoxy-lower alkyl, *e.g.*, 2-methoxyethyl, 18-0-methyl-reserpate, N,N-di-lower alkyl-amino-lower alkyl, *e.g.*, 2-dimethylaminoethyl, 18-0-methyl-deserpidate or N,N-di-lower alkyl-amino-lower alkyl, *e.g.*, 2-dimethylaminoethyl, 18-0-methyl-reserpate, as well as the corresponding 18-0 ethyl, 18-0 n-propyl, 18-0-n-butyl, 18-0-isobutyl, 18-0-n-pentyl analogs thereof and the like. Other 18-0-lower alkyl-deserpidates, especially 18-0-methyl-derivatives, are those of lower alkyl, *e.g.*, methyl, ethyl, n-propyl or n-butyl and the like, 2-lower alkoxy-ethyl, *e.g.*, 2-methoxy-ethyl, or 2-N,N-di-lower alkyl-amino-ethyl, *e.g.*, 2-N,N-

dimethylaminoethyl, esters of 9-methyl-deserpidic acid, 11-methyl-deserpidic acid, 9-methoxy-deserpidic acid, 10-methoxy-deserpidic acid, 10-methoxy-reserpic acid, 11-ethoxy-deserpidic acid, 11-n-propyloxy-deserpidic acid, 11-iso-propyloxy-deserpidic acid, 11-n-butyloxy-deserpidic acid, 10, 11-methylenedioxy-deserpidic acid, 10-benzyloxy-deserpidic acid, 11-benzyloxy-deserpidic acid, 11-methylmercapto-deserpidic acid, 11-ethylmercapto-deserpidic acid, 10-chloro-deserpidic acid, 5-methyl-reserpic acid, 6-methyl-deserpidic acid, 6-methyl-reserpic acid, 17-desmethoxy-17-ethoxy-reserpic acid, 17-desmethoxy-17-n-propyloxy-reserpic acid or 17-desmethoxy-17-isopropyloxy-reserpic acid and the like.

The compounds of this invention may be used as medicaments in the form of pharmaceutical preparations, which contain the new compounds or salts thereof in admixture with a pharmaceutical organic, or inorganic solid or liquid carrier suitable for enteral, *e.g.*, oral, or parenteral administration. For making up the preparations there can be employed substances which do not react with the new compounds, such as water, gelatine, lactose, starches, stearic acid, magnesium stearate, stearyl alcohol, talc, vegetable oils, benzyl alcohols, gums, waxes, propylene glycol, polyalkylene glycols or any other known carrier for medicamente. The pharmaceutical preparation may be solid form, for example, as solutions, suspensions or emulsions. If desired, they may contain auxiliary substances such as preserving agents, stabilizing agents, wetting or emulsifying agents, salts for varying the osmotic pressure or buffers. They may also contain, in combination, other therapeutically useful substances.

The 18-O-R_3-derivatives of lower alkyl, lower alkoxy-lower alkyl or tertiary amino-lower alkyl deserpidates, in which R_3 represents hydrocarbon, particularly lower alkyl, may be formed by reacting a compound of the formula shown in Fig. 2 of the drawings in which R_1, R_2, R_4, R_5, R_6, R_7, R_4' and R_5'' have the above-given meaning, or a salt thereof, with a lower aliphatic diazo-hydrocarbon or a substituted lower aliphatic diazo-hydrocarbon derivative in the presence of a strong inorganic Lewis acid, and, if desired, converting a resulting salt into the free base, and/or, if desired, converting a free base into a salt thereof.

Salts of the deserpidates used as the starting materials are addition salts with acids, primarily those with inorganic acids. Advantageously, those with the strong inorganic Lewis acids catalyzing the etherification reaction, *e.g.*, fluoboric acid, are used ; they may also be formed *in situ* upon addition of the Lewis acid to the reaction mixture.

The lower alkyl, lower alkoxy-lower alkyl or tertiary amino-lower alkyl deserpidates or salts thereof are reacted with the diazo compound, *e.g.*, lower diazo-alkane, lower alkoxy-lower diazo-alkane or tertiary amino-lower diazo-alkane, in the presence of a strong inorganic Lewis acid. Preferred Lewis acids contain (if desired, apart from others) the elements fluorine and/or boron : they are represented, for example, by fluoboric acid, which may be used in the form of a concentrated aqueous solution (for example, a 12 N to 16 N solution) or boron trifluoride, for example, in the form of its etherate with diethyl ether. In view of the salt-forming properties of the diserpidic acid ester, the Lewis acid, which catalyzes the etherification of the 18-hydroxyl group, is used in excess of one mole ; an about one to about two hundred, preferably an about ten to about fifty, per cent. excess appears to be sufficient to promote the etherification reaction.

The reaction is carried out according to standard etherification procedures ; solvents are preferably inert towards the reaction reagents and are represented, for example, by halogenated lower aliphatic hydrocarbons, *e.g.*, methylene chloride, ethers, *e.g.*, diethylether or tetrahydrofuran, or more polar solvents, such as, for example, lower alkyl lower alkanoates, *e.g.*, ethyl acetate, or acetonitrile and the like, as well as mixtures of such solvents. A solution of the diazo reagent in an inert solvent, such as an ether, *e.g.*, diethyl-ether, or a halogenated hydrocarbon, *e.g.*, methylene chloride, or a mixture thereof, may be added to the mixture of a deserpidic acid ester and a Lewis acid, preferably kept in solution. The diazo compound may also be distilled out of its solution into the solution of the mixture of the deserpidic acid ester and the Lewis acid. Furthermore, the mixture may also be given to the solution of the diazo reagent.

The reaction may be carried out at room temperature ; however, cooling of the reaction mixture to below room temperature, for example, to from about 10° to about —20°, especially to from about 0° to about —15°, may be advantageous. If necessary, the reaction may be carried out in the atmosphere of an inert gas, *e.g.*, nitrogen

An excess of the diazo reagent present at the end of the reaction may be destroyed, for example, by adding an acid, preferably an esterifiable carboxylic acid, *e.g.*, acetic or benzoic acid.

The desired product may be isolated according to standard procedures, *e.g.*, extraction, adsorption and elution, crystallization, etc. and purified, for example, by recrystallization, if necessary, after treatment of a solution thereof with an adsorbent, *e.g.*, aluminum oxide, charcoal, diatomaceous earth and the like.

The lower alkyl, lower alkoxy-lower alkyl or tertiary amino-lower alkyl deserpidates used as the starting materials are known or, if new, may be prepared according to procedures used for known analogs. For example, deserpidic aciads may be esterified by treatment with a lower diazo-alkane, a lower alkoxy-lower diazo-alkane or a tertiary amino-lower diazo-alkane, or by alcoholysis of deserpidic acid (16.— 18)-lactones with alkali metal compounds of lower alkanols, lower alkoxy-lower aklanols or tertiary amino-lower alkanols.

Thus, to a solution of the diazo reagent in an inert solvent, such as an ether, particularly diethylether, may be added a free deserpidic acid compound, which is preferably kept in a suspension or a solution, for example, with a lower alkanol, *e.g.*, methanol or ethanol, or a halogenated aliphatic hydrocarbon, *e.g.*, chloroform. Or, the diazo compound may be distilled out of a solution, such as a diethylether solution, into the suspension or solution of a deserpidic acid. An excess of the diazo derivative present in the reaction mixture may be destroyed, for example, by adding an additional carboxylic acid, *e.g.*, acetic or benzoic acid. The esterification may be carried out under cooling or at room temperature, and, if desired, under the atmosphere of an inert gas, *e.g.*, nitrogen.

Or by treating the necessary amount of an alkali metal, *e.g.*, lithium, potassium, or particularly sodium, with a lower alkanol, a lower alkoxy-lower alkanol or a tertiary amino-lower alkanol and adding a deserpidic acid lactone to the resulting alkali metal derivative of the alcohol, the desired deserpidate may be obtained. Although this reaction may proceed under cooling or at room temperature, the mixture is advantageously heated, if necessary, in the atmosphere of an inert gas, *e.g.*, nitrogen.

The compounds of this invention are obtained in the form of the free bases or the salts thereof. A salt may be converted into the free base, for example, by reaction with an aqueous basic reagent, such as, for example, aqueous ammonia. A free base may be converted into its therapeutically useful acid addition salts by reaction with one of the inorganic or organic acids outlined hereinbefore, for example, by treating a solution of the base in a lower alkanol, *e.g.*, methanol, or in a lower alkyl lower alkanoate, *e.g.*, ethyl acetate, with the acid or a solution thereof. Mono- or poly-salts may be formed, depending on the number of salt-forming groups and/or the conditions of salt formation.

The invention also comprises any modification of the process wherein a compound obtainable as an intermediate at any stage of the process is used as starting material and the remaining step(s) of the process is (are) carried out, as well as any new intermediates.

In the process of this invention such starting materials are preferably used which lead to final products mentioned in the beginning as preferred embodiments of the invention.

The following examples will serve to illustrate the invention ; they are not to be construed as being limitations thereof. Temperatures are given in degrees Centigrade.

EXAMPLE 1

To a solution of 2·48 g. of methyl reserpate in 400 ml. of methylene chloride, maintained at —10 to —15°, is added 66 ml. of a fluoboric acid solution while stirring. (The latter is prepared as follows : Commercially available fifty per cent. aqueous fluoboric acid is concentrated by partial evaporation under reduced pressure to an approximately 14 N solution, determined by titration with a standard sodium hydroxide solution. A stock solution of approximately 0·1 N strength is prepared by dissolving 1 ml. of the concentrated fluoboric acid in a mixture of 110 ml. of absolute ether and 30 ml. of methylene chloride.) A small precipitate forms

during the addition, which represents, probably, a salt of methyl reserpate with the acid.

A solution of diazomethane in methylene chloride (69 ml. of a 0·348 N solution) is added to the stirred reaction mixture over a period of about five minutes, whereby the temperature is maintained at —10°. The previously-mentioned precipitate dissolves again. An additional 1 ml. of the stock solution of fluoboric acid is given to the reaction mixture, and the solution is stirred for a few more minutes. 2 ml of glacial acetic acid is added with the intent to destroy any excess of diazomethane.

A solution is washed twice with five per cent. aqueous sodium carbonate and once with saturated aqueous sodium chloride, the organic layer is dried over anhydrous sodium sulfate and evaporated under reduced pessure, whereupon 2·24 g. of a tan, solid material can be recovered. As much as possible of the residue is dissolved in 50-60 ml. of benzene at room temperature: the undissolved material, representing methyl reserpate, is filtered off. The filtrate is chromatographed on about 40g. of aluminum oxide (Woelm, neutral, activity I); the desired metyl 18·0-methyl-reserpate is eluted with benzene, containing 0·2 per cent. of methanol. The oily, yellow solid is washed with cold ether and recrystallized from a 1:3-mixture of benzene and cyclohexane, using charcoal as a decolorizing agent, m.p. 228-231° (with decomposition).

Example 2

Substitution of the diazomethane solution in Example 1 by 113 ml. of a 0·212 N solution of diazoethane, adding said soultion to the mixture of methyl reserpate and fluoboric acid over a period of ten minutes and working up the reaction mixture as shown in Example 1, results in the formation of methyl 18·0-ethyl-reserpate which, after recrystallization from a 1:3-mixture of benzene and cyclohexane in the presence of charcoal, melts at 221-222·5° (with decomposition).

Example 3

The n-propyl 18·0-methyl-reserpate may be prepared by reaction n-propyl reserpate with diazomethane in the presence of fluoboric acid according to the procedure described in Example 1.

The starting material may be preared as follows:

The gaseous n-diazopropane is distilled from its ether solution into a suspension of 20 g. of reserpic acid in a 1:1-mixture of chloroform and ethanol. Any excess of n-diazopropane is decomosed with acetic acid, the solvents are evaporated under reduced pressure and the residue is poured into 800 ml. of water containing 20 ml. of concentrated aqueous ammonia. A white crystalline precipitate is obtained, which is washed with water to yield the n-propyl reserpate, m.p. 164-166°.

Instead of using methyl or n-propyl reserpate other lower alkyl, *e.g.*, methyl, ethyl, n-propyl, isopropyl, n-butyl, etc. deserpidates may be used as starting materials; they may be obtained, as shown above, by esterifying deserpidic acids with lower diazoalkanes, *e.g.*, diazomethane, diazoethane, n-diazopropane, n-diazobutane and the like. Deserpidic acids to be esterified may be, for example, deserpidic acid, 9-methyl-deserpidic acid, 11-methyl-deserpidic acid, 9-methoxy-deserpidic acid, 10-methoxy-deserpidic acid, 10-methoxy-reserpic acid, 11-ethoxy-deserpidic acid, 11-n-propyloxy deserpidic acid, 11-isopropyloxy-deserpidic acid, 11-n-butyloxy-deserpidic acid, 10,11-methylenedioxy-deserpidic acid, 10-benzyloxy-deserpidic acid, 11-benzyloxy-deserpidic acid, 11-methylmercapto-deserpidic acid, 11-ethylmercapto-deserpidic acid, 10-chloro-deserpidic acid, 5-methyl-reserpic acid, 6-methyl-deserpidic acid, 6-methyl-reserpic acid, 17-desmethoxy-17-ethoxy-reserpic acid, 17-desmethoxy-17-n-propyloxy-reserpic acid or 17-desmethoxy-17-isopropyloxy-reserpic acid, apart from reserpic acid. Upon reaction with lower diazo-alkanes, *e.g.*, diazomethane, diazoethane, n-diazopropane and the like, in the presence of fluoroboric acid or another Lewis acid according to the procedure described in the previous examples these lower alkyl deserpidates furnish the corresponding lower alkyl 18·0-lower alkyl deserpidates.

Example 4

By reacting 2-methoxyethyl reserpate with diazomethane in the presence of fluoroboric acid according to the procedure given in Example 1, the 2-methoxyethyl 18·0-methyl-reserpate may be obtained.

The starting material may be prepared as follows: To a mixture of 226 g. of a 33 per cent. aqueous solution of 2-methoxy-ethylamine and 150 ml of diethyl ether, kept at 5° to 10° in an ice bath, is added dropwise 54 g. of ethyl chloroformate. 100 g. of a cold 40 per cent. aqueous solution of sodium hydroxide and a second portion of 54 g. of ethyl chloroformate are given to the mixture, which is stirred for one hour. The ether layer is separated, the aqueous phase is extracted with 100 ml. of diethyl ether, and the two ether solutions are combined and dried over potassium carbonate. The solvent is evaporated under reduced pressure and the ethyl N-(2-methoxyethyl)-carbamate is distilled at 105-106°/17·20 mm.

To a solution of 33 g. of ethyl N-(2-methoxyethyl)-carbamate in 200 ml. of diethyl ether are added 25 g. of cracked ice and a solution of 81 g. of sodium nitrate in 125 ml. of water. While keeping the temperature below 15°, 150 g. of 35 per cent aqueous nitric acid is added carefully over a period of one hour. The ether layer is separated, washed with water and aqueous potassium carbonate and then dried over potassium carbonate. The residue, obtained after evaporation of the solvent under reduced pressure, represents the ethyl N-(2-methoxyethyl)-N-nitroso-carbamate, which is used without further purification.

A gently refluxing solution of 5 g. of potassium hydroxide in 15 g. of methanol and 150 ml. of diethyl ether is treated with a solution of 15·5 g. of ethyl N-(2-methoxyethyl)-N-nitroso-carbamate in 50 ml. of diethylether, which is added dropwise over a period of one hour. After refluxing for 5 minutes 100 ml. of water is added and the yellow ether solution, containing the 2-methoxy-diazoethane, is separated.

The above ether solution of 2-methoxy-diazoethane is reacted with small portions of a slurry of reserpic acid in methanol until no further reaction can be observed. A few drops of acetic acid are added, the solution is evaporated under reduced pressure and the residual oil is dissolved in ethyl acetate. Upon addition of petroleum ether a precipitate is formed, which is filtered off, dissolved in methylene chloride, which soution is washed with aqueous ammonia and filtered through a small column containing a diatomaceous earth. The residue, obtained after evaporation of the solvent is crystallized from ethyl acetate to yield the 2-methoxyethyl reserpate, m.p. 183-185°.

Instead of 2-methoxyethyl reserpate, other lower alkoxy-lower alkyl deserpidates may be used as the starting materials; they may be obtained according to the above-given procedure by using different deserpidic acids such as, for example, deserpidic acid, 9-methyl-deserpidic acid, 11-methyl-deserpidic acid, 9-methoxy-deserpidic acid, 10-methoxy-deserpidic acid, 10-methoxy-reserpic acid, 11-ethoxy-deserpidic acid, 11-n-propyloxy-deserpidic acid, 11-n-butyloxy-deserpidic acid, 10,11-methyelnedioxy-deserpidic acid, 10-benzyloxy-deserpidic acid, 11-benzyloxy-deserpidic acid, 11-methyl-mercapto-deserpidic acid, 11-ethylmercapto-deserpidic acid, 10-chloro-deserpidic acid, 5-methyl-reserpic acid, 6-methyl-deserpidic acid, 6-methyl-reserpic acid, 17-desemethoxy-17-ethoxy-reserpic acid, 17-desemethoxy-17-n-propyloxy-reserpic acid or 17-desmethoxy-17-isopropyloxy-reserpic acid, apart from reserpic acid. Upon reaction with lower alkoxy-lower diazoalkanes, *e.g.*, 2-methoxy-diazoethane or 2-ethoxy-diazoethane, these deserpidic acids yield the desired lower alkoxy-lower alkyl, *e.g.*, 2-methoxy-ethyl or 2-ethoxy-ethyl, deserpidates, which can be converted to the lower alkoxy-lower alkyl, *e.g.*, 2-methoxy-ethyl or 2-ethoxy-ethyl, 18·0-lower alkyl-deserpidates by reaction with lower diazo-alkanes, *e.g.*, diazomethane, diazoethane, n-diazopropane and the like, in the presence of a fluobric acid or another Lewis acid according to the proceduro outlined in Example 1.

Example 5

Upon reacting methyl deserpidate with diazomethane in the presence of fluoboric acid and a mixture of ether and methylene chloride as a solvent and working up the reaction mixture according to the procedure given in Example 1, the methyl 18·0-methyl-deserpidate can be isolated.

Other lower alkyl, *e.g.*, ethyl or n-propyl and the like, deserpidates may be reacted with lower diazo-alkanes, *e.g.*, diazomethane, diazoethane, n-diazopropane and the like, to yield other lower, *e.g.*, ethyl or n-propyl, 18·0-lower alkyl-deserpidates, *e.g.*, 18·0-ethyl-deserpidate or 18·0-n-propyl-deserpidate.

EXAMPLE 6

The 2-dimethylaminoethyl 18-0-methyl-reserpate may be formed by reacting 2-dimethylaminoethyl reserpate with 2-dimethylamino-diazoethane in the presence of fluoboric acid according to the procedure given in Example 1.

The starting material used in the above reaction may be prepared as follows: A mixture of 88 g. of a 33 per cent. aqueous N,N-dimethyl-ethylenediamine solution and 150 ml. of ether is cooled to 5° and a total of 108·5 g. of ethyl chloroformate is added in portions. A solution of 40 g. of sodium hydroxide in 60 ml. of water is given to the reaction mixture simultaneously with the second half of the ethyl chloroformate; stirring is continued for an additional hour. The ether layer is separated, the aqueous portion is extracted with ether and the ether extracts are combined and dried over anhydrous potassium carbonate. The ether is evaporated, the residue is distilled, b.p. 118-122° at 17-20 mm., to yield the ethyl N-(2-dimethylaminoethyl) carbamate

A solution of 40 g. of ethyl N-(2-dimethylamino-ethyl)-carbamate in 125 ml. of methylene chloride is cooled to 0°, and 19·5 g. of nitrosyl chloride in 300 ml. of methylene chloride is added over a period of approximately one hour while stirring and keeping the temperature between 0° and 5°. Stirring is continued for an additional two hours, the precipitate is filtered off and recrystallized from ethyl acetate to yield ethyl N-(2-dimethylaminoethyl) N-nitrosocarbamate hydrochloride, m.p. 133-135°.

A suspension of 11·3 g. of ethyl N-(2-dimethylaminoethyl)-N-nitroso-carbamate hydrochloride in 100 ml. of ether is added to a mixture of 40 g. of a 25 per cent. methanol solution of ptassium hydroxide and 300 ml. of ether while gently refluxing. After fifteen minutes of additional heating the ether layer, containing the 2-dimethylamino-diazoethane, is decanted and immediately used.

To the above-described ether solution is added portionwise 12·0 g. of reserpic acid in methylene chloride and methanol. The mixture is allowed to stand overnight at room temperature, the solvents are evaporated under reduced pressure, and the residue is added to 400 ml. of water containing 20 ml. of ammonium hydroxide. The water solution is extracted with methylene chloride, the organic solution is filtered through a column containing a diatomaceous earth and evaporated. The 2-dimethylaminoethyl reserpate is recrystallized from a mixture of ethyl acetate and petroleum ether, m.p. 110-114°.

Instead of using 2-dimethylamino-diazoethane other tertiary amino-lower diazoalkanes, *e.g.*, 2-diethylamino-diazoethane, 3-dimethylamino-diazopropane, 2-piperidino-(N)-diazoethane or 2-morpholino-(N)-diazoethane may be used to esterify reserpic acid; other deserpidic aicds, which may be esterified with the 2 dimethylamino-diazoethane or the above mentioned diazo compounds are, for example, deserpidic acid, 9-methyl-deserpidic acid, 11-methyl-deserpidic acid, 9-methoxy-deserpidic acid, 10-methoxy-deserpidic acid, 10-methoxy-reserpic acid, 11-ethoxy-deserpidic acid, 11-n-propyloxy-deserpidic acid, 11-isopropyloxy-deserpidic acid, 11-n-butyloxy-deserpidic acid, 10,11-methylenedioxy-deserpidic acid, 10 benzyloxy-deserpidic acid, 11-benzyloxy-deserpidic acid, 11-methylmercapto-deserpidic acid, 11-ethylmercapto-deserpidic acid, 10-chloro-deserpidic acid, 5-methyl-reserpic acid, 6-methyl-deserpidic acid, 6-methyl-reserpic acid, 17-desmethoxy-17-ethoxy-reserpic acid, 17-desmethoxy-17-n-propyloxy-reserpic acid or 17-desmethoxy-17-isopropyloxy-reserpic acid. The resulting tertiary amino-lower alkyl deserpidates may then be reacted with a lower diazoalkane, *e.g.*, diazomethane, diazoethane, n-diazopropane and the like, in the presence of fluoboric acid according to the procedure shown in Example 1 and the desired tertiary amino-lower alkyl 18-0-lower alkyl-deserpidates are formed.

EXAMPLE 7

Ethyl reserpate, when reacted with diazomethane in the presence of fluoboric acid according to the procedure of Example 1, may be converted to ethyl 18-0-methyl reserpate.

Other lower alkyl 18-0-lower alkyl-reserpates, prepared according to the previously-given procedure, are, for example, methyl 18-0-n-propyl-reserpate, methyl 18-0-n-butyl-reserpate, ethyl 18-0-methyl reserpate, ethyl 18-0-n-propyl-reserpate, ethyl 18-0-n-butyl reserpate, n-propyl 18-0-methyl-reserpate, n-propyl 18-0-ethyl-reserpate, n-propyl 18-0-n-butyl-reserpate, n-butyl 18-0-methyl-reserpate, n-butyl 18-0-ethyl reserpate, n-butyl 18-0-n-propyl-reserpate, n-hexyl 18-0-methyl-reserpate, n-hexyl 18-0-ethyl-reserpate and the like.

EXAMPLE 8

The reaction of methyl reserpate with 2-methoxy-diazoethane in the presence of fluoboric acid according to the procedure of Example 1 may yield the desired methyl 18-0-(2-methoxyethyl)-reserpate.

When reacted with 2-dimethylamino-diazoethane in the presence of fluoboric acid, methyl reserpate may furnish the desired methyl 18-0-(2-dimethylaminoethyl)-reserpate.

A modification of the above procedure, comprises reacting a deserpidic acid of the formula shown in Fig. 3 of the drawings in which R_2, R_4, R_5, R_6, R_7, R_8' and R_9'' have the above-given meaning, with a diazo-compound, such as, for example, a lower diazo-alkane, a lower alkoxy-lower diazo-alkane or a tertiary amino-lower diazo-alkane, and isolating a deserpidate compound of the formula shown in Fig. 4 of the drawings in which R_1, R_2, R_4, R_5, R_6, R_7, R_8' and R_9'' have the above-given meaning.

This reaction may be carried out according to the previously-given procedures and is catalyzed by the necessary amount of one of the Lewis acid outlined hereinbefore. It may be advantageous to carry out the reaction in such manner that first the reactive carboxyl group in the 16-position is esterified. This may be done by adding part (one mol or an excess) of the diazo-reagent to the deserpidic acid compound, using appropriate solvents, and, after the addition of the necessary Lewis acid, giving to the reaction mixture the second part (one mol or an excess) of the diazo-reagent.

The compounds of this invention may also be prepared by treating deserpidates of the formula shown in Fig. 5 of the drawings in which R_1, R_2, R_4, R_5, R_6, R_7, R_8' and R_9'' have the previously-given meaning, and R_8' represents a reactive, esterified hydroxyl group, with an alkali metal compound of an alcohol of the formula R_3-OH, in which R_3 has the previously-given meaning

A reactive esterified hydroxyl group is primarily a hydroxyl group esterified with a strong inorganic acid, especially a mineral acid, such as a hydrohalic acid, particularly hydrobromic or hydroiodic acid. In the above-depicted starting materials, R_8', stands, therefore, advantageously for halogen, particularly for bromine or iodine.

The reactive ester group, upon treatment with an alkali metal compound of an alcohol of the formula R_3-OH, is being exchanged for an ether group, represented by the radical R_3-O-, in which R_3 has the previously-given meaning. Such alkali metal, *e.g.*, lithium, sodium or potassium, compounds of alcohols, particularly of lower alkanols, lower alkoxy-lower alkanols or tertiary amino-lower alkanols, are known and may be prepared according to known procedures, for example, by reacting the alcohol with the alkali metal. The reaction of the metal reagent with the deserpidate compound may be carried out under known conditions, preferably in the presence of an inert solvent, for example, an alcohol, *e.g.*, a lower alkanol, such as the alchol used for the preparation of the alkali metal reagents described hereinabove. In this reaction, certain transesterification of the esterified carboxyl group in the 16 position of the deserpidate molecule may occur; in the final products R_1 and R_3 may, therefore, have identical meaning.

The starting materials used in the above reaction are known, or, if new, may be prepared according to the methods used for the manufacture of the known analogs. For example, upon treating a lower alkyl deserpidate, *e.g.*, methyl deserpidate, with a p-toluene sulfonyl halide, particularly p-toluene sulfonyl chloride, for example, in the presence of an organic base, *e.g.*, pyridine, the lower alkyl, *e.g.*, methyl, 18-0-(p-toluene sulfonyl)-deserpidate may be formed. The latter, when reacted with an alkali metal halide, *e.g.*, lithium, sodium or potassium bromide or iodide, in the presence of an inert solvent, *e.g.*, acetonitrile and the like, may be converted to the desired lower alkyl 18-desoxy-18-halogen-deserpidate.

Sd./- B. DEPENNING.

DE DEPENNING & DEPENNING,

Agents for the Applicants.

Dated this 29th day of December 1960.

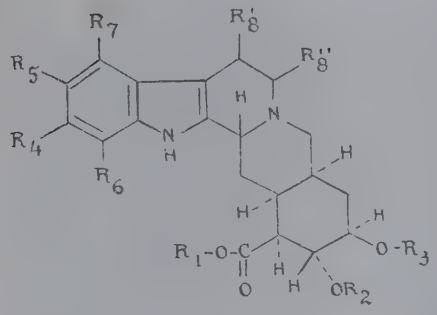

FIG. 1

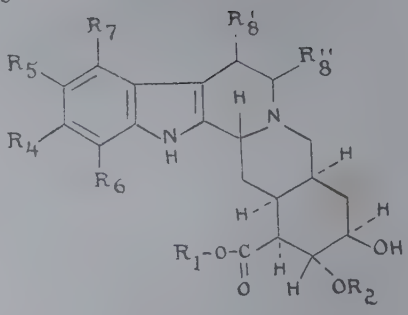

FIG. 2

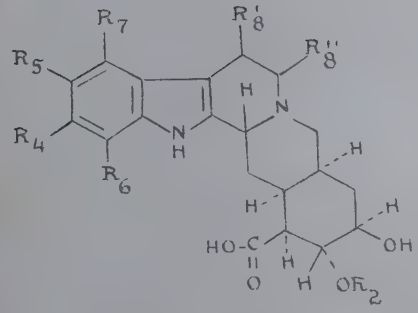

FIG. 3

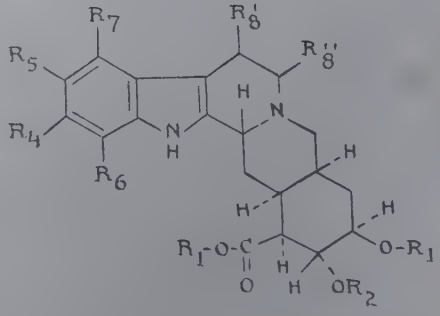

FIG. 4

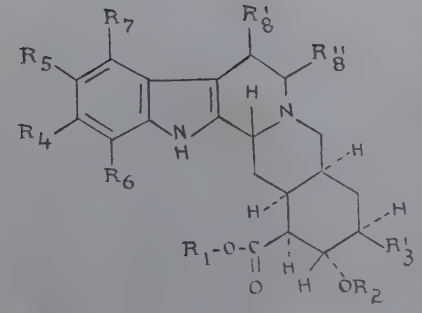

FIG. 5

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PROVISIONAL SPECIFICATION.

PHARMACEUTICAL PREPARATIONS CONTAINING NEW 18-ALIPHATIC ETHERS OF 17-LOWER ALKOXY-18-HYDROXY-3-EPI-ALLOYOHIMBANE-16-CARLOXYLIC ACID ESTERS.

CIBA LIMITED, Chemical Manufacturers, a Swiss Corporation, of 141, Klybeckstrasse, Basle, Switzerland.

The following specification describes the nature of this invention.

The present invention concerns ethers of deserpidates. More particularly, it relates to 18-O-ethers of deserpidates having the formula shown in Fig. 1 of the accompanying drawings, in which R_1 represents lower alkyl, lower alkoxy-lower alkyl or tertiary amino-lower alkyl, R_2 stands for lower alkyl, R_3 represents a lower aliphatic hydrocarbon or a substituted lower aliphatic hydrocarbon radical, R_4 stands for hydrogen, lower alkyl, lower alkoxy, monocyclic carbocyclic aryl-lower alkoxy, lower alkyl-mercapto or halogen, each of the substituents R_5, R_6 and R_7 represents primarily hydrogen, or one of the substituents characteristic of R_4, whereby two neighbouring substituents, when taken together, may also form a lower alkylenedioxy radical, and each of the radicals R_8' and R_8'' represents hydrogen or lower alkyl, and salts thereof, and process for the preparation of such compounds.

A lower alkyl group R_1 stands, for example, for methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, isopentyl, n-hexyl and the like.

In a lower alkoxy-lower alkyl group R_1, the lower alkoxy portion may be, for example, methoxy, ethoxy, n-propyloxy, isopropyloxy and the like. The tertiary amino group of a tertiary amino-lower alkyl radical R_1 is primarily an N,N-di-lower alkyl-amino group, in which lower alkyl contains from one to four carbon atoms, *e.g.* dimethylamino, diethylamino, di-n-propylamino or di-isopropylamino and the like, an N,N-lower alkylene-imino group, in which lower alkylene contains from four to six carbon atoms, *e.g.*, pyrrolidino, piperidino or hexamethyleneimino, an N,N-lower oxa-alkylene-imino group, in which lower oxa-alkylene contains, preferably, four carbon atoms, *e.g.* morpholino, or an N,N-lower aza-alkylene-imino group, in which lower aza-alkylene contains, preferably, four carbon atoms, *e.g.* N-methyl-piperazino.

The lower alkyl portion of a lower alkoxy-lower alkyl radical R_1 or a tertiary amino-lower alkyl radical R_1 is represented by a lower alkylene radical, which separates the lower alkoxy group or the tertiary amino group from the carbonyl portion of the carboxyl group by at least two, preferably by two to three, carbon atoms. Such radicals are primarily 1,2-ethylene, 1-methyl-1, 2-ethylene or 2-methyl-1, 2-ethylene or 1,3-propylene; other lower alkylene radicals may be 1,4-butylene or 1-methyl-1, 3-propylene and the like.

The lower alkyl group R_2 may stand for ethyl, propyl, isopropyl, but represents above all methyl.

Generally, R_3 represents a lower aliphatic hydrocarbon or a substituted lower aliphatic hydrocarbon radical; substituted lower aluphatic hydrocarbon radicals may contain as functional groups lower alkoxy, tertiary amino and the like. R_3 represents, primarily, lower alkyl, such as, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, isopentyl or n-hexyl and the like. These radicals may contain as functional groups lower alkoxy, *e.g.* methoxy or ethoxy and the like, tertiary amino-lower alkyl, such as N,N-di-lower alkyl-amino, *e.g.* N,N-dimethylamino, N-ethyl-N-methyl-amino, N,N-dietylamino and the like, N,N-lower alkylene-imino, in which alkylene contains, primarily, from four to six carbon atoms, *e.g.* pyrrolidino, piperidino, hexamethylene-imino and the like, N,N-lower oxa-alkylene-imino, in which alkylene contains, primarily, four carbon atoms, *e.g.* morpholino, N,N-lower aza-alkylene-imino, in which alkylene contains, primarily, four carbon atoms, *e.g.* 4-methyl-piperazino and the like. Preferably, these substituents are separated from the oxygen atoms of the 18-position of the deserpidate nucleus by at least two, advantageously, by two to three, carbon atoms. Substituted lower aliphatic hydrocarbon radicals, representing R_3, are, therefore, 2-lower alkoxy-ethyl, *e.g.* 2-methoxy-ethyl or 2-ethoxy-ethyl, 3-lower alkoxy-propyl, *e.g.* 3-methoxy-propyl, 2-N,N-di-lower alkyl-amino-ethyl, e.g. 2-dimethylaminoethyl or 2-diethylaminoethyl, 3-N,N-di-lower alkyl-amino-propyl, *e.g.* 3-dimethylamino-propyl, or 2-N,N-lower alkylene-imino-ethyl *e.g.* 2-(1-piperidino)-ethyl, or 3-N,N-lower alkylene-imino-propyl, *e.g.* 3-(1-pyrrolidino)-propyl, and the like.

The substituent R_4 represents primarily hydrogen or lower alkoxy, *e.g.* ethoxy, n-propyloxy, isopropyloxy, or particularly methoxy. It may also stand for monocyclic carbocyclic aryl-lower alkoxy, *e.g.* benzyloxy, lower alkyl-mercapto, *e.g.* ethyl-mercapto or ethylmercapto, lower alkyl, *e.g.* methyl or ethyl, or halogen, *e.g.* fluorine, chlorine or bromine. The substituents R_5, R_6 and R_7 represent primarily hydrogen; they may also stand for the substituents characteristic for R_4, such as, for example, lower alkyl, *e.g.* methyl or ethyl, lower alkoxy, *e.g.* methoxy or ethoxy, or halogen, *e.g.* chlorine or bromine. Furthermore, two neighbouring substituents selected from R_4, R_5, R_6 and R_7, when taken together may form a lower alkylenedioxy, *e.g.* methylenedioxy, radical.

Each of the radicals R_8' and R_8'' stands, preferably, for hydrogen; when representing lower alkyl, such radical may stand for ethyl, or primarily for methyl.

Salts of the new compounds of this invention are pharmaceutically acceptable addition salts with acids, primarily with inorganic acids, such as mineral acids, *e.g.* hydrochloric, hydrobromic, sulfuric or phosphoric acid and the like, or with strong, organic acids, *e.g.* acetic, hydroxy-acetic or methane sulfonic acid and the like.

The new compounds of this invention have sedative and tranquilizing effects on the central nervous system; they may also exhibit antihypertensive properties. Furthermore, tests show that animals, treated with the compounds of the present invention, recover faster and more completely from the pharmacological effects than those treated with known, naturally occurring Rauwolfia alkaloids, such as reserpine, deserpidine or rescinnamine. In addition, certain quantitative differentiations may be observed within the group of the new compounds of this invention. Thus, when compared with the established ratio existing between antihypertensive and sedative effects in the above-mentioned natural Rauwolfia alkaloids some of the compounds of this invention have more predominant sedative effects with negligible antihypertensive activity, whereas in others, the latter effect may be more pronounced than the sedative and tranquilizing component.

The compounds of the present invention may, primarily, be used as sedative agents to relieve states of hyperactivity, tension and agitation as, for example, associated with mental disturbances. Compounds with predominating antihypertensive effect may also be employed as antihypertensive agents to relieve hypertensive conditions as, for example, benign or malignant hypertension, renal hypertension or hypertension associated with pregnancy, such as toxemia of pregnancy.

The above-described properties are particularly exhibited by lower alkyl, 2-lower alkoxy-ethyl or 2-N,N-di-lower alkyl-amino-ethyl 11-R_4-18-O-R_3-deserpidates, in which R_4 stands for lower alkyl, especially methyl, and R_4 for hydrogen or methoxy. Representing this group of compounds are lower alkyl, *e.g.* methyl, ethyl, n-propyl or n-butyl, 18-O-methyl-deserpidate or lower alkyl, *e.g.* methyl, ethyl, n-propyl or n-butyl, 18-O-methyl-reserpate, lower alkoxy-lower alkyl, *e.g.* 2-methoxyethyl, 18-O-methyl-deserpidate, lower alkoxy-lower

alkyl, *e.g.* 2-methoxyethyl, 18-O-methyl-reserpate. N,N-di-lower alkyl-amino-lower alkyl, *e.g.* 2-dimethylaminoethyl, 18-O-methyl-deserpidate or N,N-di-lower alkyl-amino-lower alkyl, *e.g.* 2-dimethylaminoethyl, 18-O-methyl-reserpate, as well as the corresponding 18-O-ethyl, 18-O-n-propyl, 18-O-n-butyl, 18-O-isobutyl, 18-O-n-pentyl analogs thereof and the like. Other 18-O-lower alkyl-deserpidates, especially 18-O-methyl-derivatives, are those of lower alkyl, *e.g.* methyl, ethyl, n-propyl or n-butyl and the like, 2-lower alkoxy-ethyl, *e.g.* 2-methoxy-ethyl, or 2-N,N-di-lower alkyl-amino-ethyl, *e.g.* 2-N,N-dimethylaminoethyl, esters of 9-methyl-deserpidic acid, 11-methyl-deserpidic acid, 9-methoxy-deserpidic acid, 10-methoxy-deserpidic acid, 10-methoxy-reserpic acid, 11-ethoxy-deserpidic acid, 11-n-propyloxy-deserpidic acid, 11-isopropyloxy-deserpidic acid, 11-n-butyloxy-deserpidic acid, 10,11-methylenedioxy-deserpidic acid, 10-benzyloxy-deserpidic acid, 11-benzyloxy-deserpidic acid, 11-methylmercapto-deserpidic acid, 11-ethylmercapto-deserpidic acid, 10-chloro-deserpidic acid, 5-methyl-reserpic acid, 6-methyl-deserpidic acid, 6-methyl-reserpic acid, 17-desmethoxy-17-ethoxy-reserpic acid, 17-desmethoxy-17-n-propyloxy-reserpic acid or 17-desmethoxy-17-isopropyloxy-reserpic acid and the like.

The compounds of this invention may be used as medicaments in the form of pharmaceutical preparations, which contain the new compounds or salts thereof in admixture with a pharmaceutical organic or inorganic, solid or liquid carrier suitable for enteral, *e.g.* oral, or parenteral administration. For making up the preparations there can be employed substances which do not react with the new compounds, such as water, gelatine, lactose, starches, stearic acid, magnesium stearate, stearyl alcohol, talc, vegetable oils, benzyl alcohols, gums, waxes, propylene glycol, polyalkylene glycols or any other known carrier for medicamente. The pharmaceutical preparation may be in solid form, for example, as solutions, suspensions or emulsions. If desired, they may contain auxiliary substances such as preserving agents, stabilizing agents, wetting or emulsifying agents, salts for varying the osmotic pressure or buffers. They may also contain, in combination, other therapeutically useful substances.

The 18-O-R_3-derivatives of lower alkyl, lower alkoxy-lower alkyl or tertiary amino-lower alkyl deserpidates, in which R_3 represents hydrocarbon, particularly lower alkyl, may be formed by reacting a compound of the formula shown in Fig. 2 of the drawings in which R_1, R_2, R_4, R_5, R_6, R_7, R_8' and R_9'' have the above-given meaning, or salt thereof, with a lower aliphatic diazo-hydrocarbon or a substituted lower aliphatic diazo-hydrocarbon derivative in the presence of a strong inorganic Lewis acid, and, if desired, converting a resulting salt into the free base, and/or, if desired, converting a free base into a salt thereof.

Salts of the deserpidates used as the starting materials are addition salts with acids, primarily those with inorganic acids. Advantageously, those with the strong inorganic Lewis acids catalyzing the etherification reaction, *e.g.* fluoboric acid, are used; they may also be formed *in situ* upon addition of the Lewis acid to the reaction mixture.

The lower alkyl, lower alkoxy-lower alkyl or tertiary amino-lower alkyl deserpidates or salts thereof are reacted with the diazo compound, *e.g.* lower diazo-alkane, lower alkoxy-lower diazo-alkane or tertiary amino-lower diazo-alkane, in the presence of a strong inorganic Lewis acid. Preferred Lewis acids contain (if desired, apart from others) the elements fluorine and/or boron; they are represented, for example, by fluoboric acid, which may be used in the form of a concentrated aqueous solution (for example, a 12N to 16N solution) or boron trifluoride, for example, in the form of its etherate with diethyl ether. In view of the salt-forming properties of the deserpidic acid ester, the Lewis acid, which catalyzes the etherification of the 18-hydroxyl group, is used in excess of one mole; an about one to about two hundred, preferably an about ten to about fifty, per cent excess appears to be sufficient to promote the etherification reaction.

The reaction is carried out according to standard etherification procedures; solvents are preferably inert towards the reaction reagents and are represented, for example, by halogenated lower aliphatic hydrocarbons, *e.g.* methylene chloride ethers, *e.g.* diethylether or tetrahydrofuran, or more polar solvents, such as, for example, lower alkyl lower alkanoates, *e.g.* ethyl acetate, or acetonitrile and the like, as well as mixtures of such solvents. A solution of the diazo reagent in an inert solvent, such as an ether, *e.g.*, diethylether, or a halogenated hydrocarbon, *e.g.* methylene chloride, or a mixture thereof, may be added to the mixture of a deserpidic acid ester and a Lewis acid, preferably kept in solution. The diazo compound may also be distilled out of its solution into the solution of the mixture of the deserpidic acid ester and the Lewis acid. Furthermore, the mixture may also be given to the solution of the diazo reagent.

The reaction may be carried out at room temperature; however, cooling of the reaction mixture to below room temperature, for example, to from about 10° to about −20°, especially to from about 0° to about −15°, may be advantageous. If necessary, the reaction may be carried out in the atmosphere of an inert gas, *e.g.* nitrogen.

An excess of the diazo reagent present at the end of the reaction may be destroyed, for example, by adding an acid, preferably an esterifiable carboxylic acid, *e.g.* acetic or benzoic acid.

The desired product may be isolated according to standard procedures, *e.g.* extraction, adsorption and elution, crystallization, etc. and purified, for example, by recrystallization, if necessary, after treatment of a solution thereof with an adsorbent, *e.g.* aluminium oxide, charcoal, diatomaceous earth and the like.

The lower alkyl, lower alkoxy-lower alkyl or tertiary amino-lower alkyl deserpidates used as the starting materials are known or, if new, may be prepared according to procedures used for known analogs. For example, deserpidic acids may be esterified by treatment with a lower diazo alkane, a lower alkoxy-lower diazo-alkane or a tertiary amino-lower diazo-alkane, or by alcoholysis of deserpidic acid (16 —> 18)-lactones with alkali metal compounds of lower alkanols, lower alkoxy-lower alkanols or tertiary amino-lower alkanols.

Thus, to a solution of the diazo reagent in an inert solvent, such as an ether, particularly diethylether, may be added a free deserpidic acid compound, which is preferably kept in a suspension or a solution, for example, with a lower alkanol, *e.g.* methanol or ethanol, or a halogenated aliphatic hydrocarbon, *e.g.* chloroform. Or, the diazo compound may be distilled out of a solution, such as a diethylether solution, into the suspension or solution of a deserpidic acid. An excess of the diazo derivative present in the reaction mixture may be destroyed, for example, by adding an additional carboxylic acid, *e.g.* acetic or benzoic acid. The esterification may be carried out under cooling or at room temperature, and, if desired, under atmosphere of an inert gas, *e.g.* nitrogen.

Or, by treating the necessary amount of an alkali metal, *e.g.* lithium, potassium, or particularly sodium, with a lower alkanol, a lower alkoxy-lower alkanol or a tertiary amino-lower alkanol and adding a deserpidic acid lactone to the resulting alkali metal derivative of the alcohol, the desired deserpidate may be obtained. Although this reaction may proceed under cooling or at room temperature, the mixture is advantageously heated, if necessary, in the atmosphere of an inert gas, *e.g.* nitrogen.

The compounds of this invention are obtained in the form of the free bases or the salts thereof. A salt may be converted into the free base, for example, by reaction with an aqueous basic reagent, such as, for example, aqueous ammonia. A free base may be converted into its therapeutically useful acid addition salts by reaction with one of the inorganic or organic acids outlined hereinbefore, for example, by treating a solution of the base in lower alkanol, *e.g.* methanol, or in a lower alkyl lower alkanoate, *e.g.* ethyl acetate, with the acid or a solution thereof. Mono- or poly-salts may be formed, depending on the number of salt-forming groups and/or the conditions of salt formation.

The invention also comprises any modification of the process wherein a compound obtainable as an intermediate at any stage of the process is used as starting material and the remaining step(s) of the process is(are) carried out, as well as any new intermediates.

In the process of this invention such starting materials are preferably used which lead to final products mentioned in the beginning as preferred embodiments of the invention.

The following example will serve to illustrate the invention; they are not to be construed as being limitations thereon. Temperatures are given in degrees Centigrade.

Example 1.

To a solution of 2.48 g. of methyl reserpate in 400 ml. of methylene chloride, maintained at −10 to −15°, is added 56 ml. of a fluoboric acid solution while stirring. (The latter is prepared as follows: Commercially available fifty per cent. aqueous fluoboric acid is concentrated by partial evaporation under reduced pressure to an approximately 14N solution, determined by titration with a standard sodium hydroxide solution. A stock solution of approximately 0.1N strength is prepared by dissolving 1 ml. of the concentrated fluoboric acid in a mixture of 110 ml. of absolute ether and 30 ml. of methylene chloride). A small precipitate forms during the addition, which represents, probably, a salt of methyl reserpate with the acid.

A solution of diazomethane in methylene chloride (69 ml. of a 0.348N solution) is added to the stirred reaction mixture over a period of about five minutes, whereby the temperature is maintained at −10°. The previously-mentioned precipitate dissolves again. An additional 1 ml. of the stock solution of fluoboric acid is given to the reaction mixture, and the solution is stirred for a few more minutes. 2 ml. of glacial acetic acid is added with the intent to destroy any excess of diazomethane.

The solution is washed twice with five per cent aqueous sodium carbonate and once with saturated aqueous sodium chloride, the organic layer is dried over anhydrous sodium sulfate and evaporated under reduced pressure, whereupon 2.24 g. of a tan, solid material can be recovered. As much as possible of the residue is dissolved in 50-60 ml. of benzene at room temperature; the undissolved material, representing methyl reserpate, is filtered off. The filtrate is chromatographed on about 40 g. of aluminum oxide (Woelm, neutral, activity I); the desired methyl 18-O-methyl-reserpate is eluted with benzene, containing 0.2 per cent of methanol. The oily, yellow solid is washed with cold ether and recrystallized from a 1:3-mixture of benzene and cyclohexane, using charcoal as a decolorizing agent, m.p. 228-231° (with decomposition).

Example 2.

Substitution of the diazomethane solution in Example 1 by 113 ml. of a 0.212 N solution of diazoethane, adding said solution to the mixture of methyl reserpate and fluoboric acid over a period of ten minutes and working up the reaction mixture as shown in Example 1, results in the formation of methyl 18-O-ethyl-reserpate which, after recrystallization from a 1:3-mixture of benzene and cyclohexane in the presence of charcoal, melts at 221-222.5° (with decomposition).

Example 3.

The n-propyl 18-O-methyl-reserpate may be prepared by reacting n-propyl reserpate with diazomethane in the presence of fluoboric acid according to the procedure described in Example 1.

The starting material may be prepared as follows: The gaseous n-diazopropane is distilled from its ether solution into a suspension of 20 g. of reserpic acid in a 1:1-mixture of chloroform and ethanol. Any excess of n-diazopropane is decomposed with acetic acid, the solvents are evaporated under reduced pressure and the residue is poured into 800 ml. of water containing 20 ml. of concentrated aqueous ammonia. A white crystalline precipitate is obtained, which is washed with water to yield the n-propyl reserpate, m.p. 164-166°.

Instead of using methyl or n-propyl reserpate other lower alkyl, *e.g.* methyl, ethyl, n-propyl, isopropyl, n-butyl, etc. deserpidates may be used as starting materials; they may be obtained, as shown above, by esterifying deserpidic acids with lower diazoalkanes, *e.g.* diazomethane, diazoethane, n-diazopropane, n-diazobutane and the like. Deserpidic acids to be esterified may be, for example, deserpidic acid, 9-methyl-deserpidic acid, 11-methyl-deserpidic acid, 9-methoxy-deserpidic acid, 10-methoxy-deserpidic acid, 10-methoxy-reserpic acid, 11-ethoxy-deserpidic acid, 11-n-propyloxy-deserpidic acid, 11-isopropyloxy-deserpidic acid, 11-n-butyloxy-deserpidic acid, 10,11-methylenedinxy-deserpidic acid, 10-benzyloxy-deserpidic acid, 11-benzyloxy-deserpidic acid, 11-methylmercapto-deserpidic acid, 11-ethylmercapto-deserpidic acid, 10-chloro-deserpidic acid, 5-methyl-reserpic acid, 5-methyl-deserpidic acid, 5-methyl-reserpic acid, 17-desmethoxy-17-ethoxy-reserpic acid, 17-desmethoxy-17-n-propyloxy-reserpic acid or 17-desmethoxy-17-isopropyloxy-reserpic acid, apart from reserpic acid. Upon reaction with lower diazo-alkanes, *e.g.*, diazomethane, diazoethane, n-diazopropane and the like, in the presence of fluoboric acid or another Lewis acid according to the procedure described in the previous examples these lower alkyl deserpidates furnish the corresponding lower alkyl 18-O-lower alkyl-deserpidates.

Example 4.

By reacting 2-methoxyethyl reserpate with diazo-methane in the presence of fluoboric acid according to the procedure given in Example 1, the 2-methoxyethyl 18-O-methyl reserpate may be obtained.

The starting material may be prepared as follows: To a mixture of 226 g. of a 33 per cent aqueous solution of 2-methoxy-ethylamine and 150 ml. of diethyl ether, kept at 5° to 10° in an ice bath, is added dropwise 54 g. of ethyl chloroformate. 100 g. of a cold 40 per cent aqueous solution of sodium hydroxide and a second portion of 54 g. of ethyl chloroformate are given to the mixture, which is stirred for one hour. The ether layer is separated, the aqueous phase is extracted with 100 ml. of diethyl ether, and the two ether solutions are combined and dried over potassium carbonate. The solvent is evaporated under reduced pressure and the ethyl N-(2-methoxyethyl)-carbamate is distilled at 105-106°/17-20 mm

To a solution of 33 g. of ethyl N-(2-methoxyethyl)-carbamate in 200 ml. of diethyl ether are added 25 g. of cracked ice and a solution of 81 g. of sodium nitrite in 125 ml. of water. While keeping the temperature below 15°, 150 g. of 35 per cent aqueous nitric acid is added carefully over a period of one hour. The ether layer is separated, washed with water and aqueous potassium carbonate and then dried over potassium carbonate. The residue, obtained after evaporation of the solvent under reduced pressure, represents the ethyl N-(2-methoxyethyl)-N-nitrosocarbamate, which is used without further purification.

A gently refluxing solution of 5 g. of potassium hydroxide in 15 g. of methanol and 150 ml. of diethyl ether is treated with a solution of 15.5 g. of ethyl N-(2-methoxyethyl)-N-nitroso-carbamate in 50 ml. of diethylether, which is added dropwise over a period of one hour. After refluxing for 5 minutes 100 ml. of water is added and the yellow ether solution, containing the 2-methoxy-diazoethane, is separated.

The above ether solution of 2-methoxy-diazoethane is reacted with small portions of a slurry of reserpic acid in methanol until no further reaction can be observed. A few drops of acetic acid are added, the solution is evaporated under reduced pressure and the residual oil is dissolved in ethyl acetate. Upon addition of petroleum ether a precipitate is formed, which is filtered off, dissolved in methylene chloride, which solution is washed with aqueous ammonia and filtered through a small column containing a diatomaceous earth. The residue, obtained after evaporation of the solvent is crystallized from ethyl acetate to yield the 2-methoxyethyl reserpate, m.p. 183-185°.

Instead of 2-methoxyethyl reserpate, other lower alkoxy-lower alkyl deserpidates may be used as the starting materials; they may be obtained according to the above-given procedure by using different deserpidic acids, such as, for example, deserpidic acid, 9-methyl-deserpidic acid, 11-methyl-deserpidic acid, 9-methoxy-deserpidic acid, 10-methoxy-deserpidic acid, 10-methoxy-reserpic acid, 11-ethoxy-deserpidic acid, 11-n-propyloxy-deserpidic acid, 11-n-butyloxy-deserpidic acid, 10,11-methylenedioxy-deserpidic acid, 10-benzyloxy-deserpidic acid, 11-benzyloxy-deserpidic acid, 11-methylmercapto-deserpidic acid, 11-ethylmercapto-deserpidic acid, 10-chloro-deserpidic acid, 5-methyl-reserpic acid, 5-methyl-deserpidic acid, 5-methyl-reserpic acid, 17-desmethoxy-17-ethoxy-reserpic acid, 17-desmethoxy-17-n-propyloxy-reserpic acid or 17-desmethoxy-17-isopropyloxy-reserpic acid, apart from reserpic acid. Upon reaction with lower alkoxy-lower diazo-alkanes, *e.g.* 2-methoxy-diazoethane or 2-ethoxy-diazoethane, these deserpidic acids yield the desired lower alkoxy-lower alkyl, *e.g.* 2-methoxy-ethyl or 2-ethoxy-ethyl, deserpidates, which can be converted to the lower alkoxy-lower alkyl, *e.g.* 2-methoxy-ethyl or 2-ethoxy-ethyl, 18-O-lower alkyl-deserpidates by reaction with lower diazo-alkanes, e.g. diazomethane, diazoethane, n-diazopro-

pane and the like, in the presence of fluoboric acid or another Lewis acid according to the procedure outlined in Example 1.

Example 5.

Upon reacting methyl deserpidate with diazomethane in the presence of fluoboric acid and a mixture of ether and methylene chloride as a solvent and working up the reaction mixture according to the procedure given in Example 1, the methyl 18-O-methyl-deserpidate can be isolated.

Other lower alkyl, *e.g.* ethyl or n-propyl and the like, deserpidates may be reacted with lower diazo-alkanes, *e.g.* diazo-methane, diazoethane, n-diazopropane and the like, to yield other lower, *e.g.* ethyl or n-propyl, 18-O-lower alkyl-deserpidates, *e.g.* 18-O-ethyl-deserpidate or 18-O-n-propyl-deserpidate.

Example 6.

The 2-dimethylaminoethyl 18-O-methyl-reserpate may be formed by reacting 2-dimethylaminoethyl reserpate with 2-dimethyl-amino-diazoethane in the presence of fluoboric acid according to the procedure given in Example 1.

The starting material used in the above reaction may be prepared as follows: A mixture of 88 g. of a 33 per cent aqueous N,N-dimethyl-ethylenediamine solution and 150 ml. of ether is cooled to 5° and a total of 108.5 g. of ethyl chloroformate is added in portions. A solution of 40 g. of sodium hydroxide in 60 ml. of water is given to the reaction mixture simultaneously with the second half of the ethyl chloroformate; stirring is continued for an additional hour. The ether layer is separated, the aqueous portion is extracted with ether and the ether extracts are combined and dried over anhydrous potassium carbonate. The ether is evaporated, the residue is distilled, b.p. 118-122° at 17-20 mm. to yield the ethyl N-(2-dimethylaminoethyl)-carbamate.

A solution of 40 g. of ethyl N-(2-dimethylaminoethyl)-carbamate in 125 ml. of methylene chloride is cooled to 0° and 19.5 g. of nitrosyl chloride in 300 ml. of methylene chloride is added over a period of approximately one hour while stirring and keeping the temperature between 0° and 5°. Stirring is continued for an additional two hours, the precipitate is filtered off and recrystallized from ethyl acetate to yield ethyl N-(2-dimethylaminoethyl)-N-nitroso-carbamate hydrochloride, m.p. 133-135°.

A suspension of 11.3 g. of ethyl N-(2-dimethylamino-ethyl)-N-nitroso-carbamate hydrochloride in 100 ml. of ether is added to a mixture of 40 g. of a 25 per cent methanol solution of potassium hydroxide and 300 ml. of ether while gently refluxing. After fifteen minutes of additional heating the ether layer, containing the 2-dimethylamino-diazoethane, is decanted and immediately used.

To the above-described ether solution is added portionwise 12.0 g. of reserpic acid in methylene chloride and methanol. The mixture is allowed to stand overnight at room temperature, the solvents are evaporated under reduced pressure, and the residue is added to 400 ml. of water containing 20 ml. of ammonium hydroxide. The water solution is extracted with methylene chloride, the organic solution is filtered through a column containing a diatomaceous earth and evaporated. The 2-dimethylaminoethyl reserpate is recrystallized from a mixture of ethyl acetate and petroleum ether, m.p. 110-114°.

Instead of using 2-dimethylamino-diazoethane other tertiary amino-lower diazoalkanes, *e.g.* 2-diethylamino-diazoethane, 3-dimethylamino-diazopropane, 2-piperidino-(N)-diazoethane or 2-morpholino-(N)-diazoethane may be used to esterify reserpic acid: other deserpidic acids, which may be esterified with the 2-dimethylamino-diazoethane or the above mention diazo compounds are, for example, deserpidic acid, 9-methyl-deserpidic acid, 11-methyl-deserpidic acid, 9-methoxy-deserpidic acid, 10-methoxy-deserpidic acids, 10-methoxy-reserpic acid, 11-ethoxy-deserpidic acid, 11-n-propyloxy-deserpidic acid, 11-isopropyloxy-deserpidic acid, 11-n-butyloxy-deserpidic acid, 10,11-methylenedioxy deserpidic acid, 10-benzyloxy-deserpidic acid, 11-benzyloxy-deserpidic acid, 11-methyl-mercapto-deserpidic acid, 11-ethyl-mercapto-deserpidic acid, 10-chloro-deserpidic acid, 5-methyl-reserpic acid, 6-methyl-deserpidic acid, 6-methyl-reserpic acid, 17-desmethoxy-17-ethoxy-reserpic acid, 17-desmethoxy-17-n-propyloxy-reserpic acid or 17-desmethoxy-17-isopropyloxy-reserpic acid. The resulting tertiary amino-lower alkyl deserpidates may then be reacted with a lower diazoalkane, e.g. diazomethane, diazoethane, n-diazopropane and the like, in the presence of fluoboric acid according to the procedure shown in Example 1 and the desired tertiary amino-lower alkyl 18-O-lower alkyl-deserpidates are formed.

Example 7.

Ethyl reserpate, when reacted with diazomethane in the presence of fluoboric acid according to the procedure of Example 1, may be converted to ethyl 18-O-methyl reserpate.

Other lower alkyl 18-O-lower alkyl-reserpates, prepared according to the previously-given procedure, are, for example, methyl 18-O-n-propyl-reserpate, methyl 18-O-n-butyl-reserpate, ethyl 18-O-ethyl-reserpate, ethyl 18-O-n-propyl-reserpate, ethyl 18-O-n-butyl-reserpate, n-propyl 18-O-ethyl-reserpate, n-propyl 18-O-n-propyl-reserpate, n-propyl 18-O-n-butyl-reserpate, n-butyl 18-O-methyl-reserpate, n-butyl 18-O-ethyl reserpate, n-butyl 18-O-n-propyl-reserpate, n-hexyl 18-O-methyl-reserpate, n-hexyl 18-O-ethyl-reserpate and the like.

Example 8.

The reaction of methyl reserpate with 2-methoxy-diazoethane in the presence of fluoboric acid according to the procedure of Example 1 may yield the desired methyl 18-O-(2-methoxyethyl)-reserpate.

When reacted with 2-dimethylamino-diazoethane in the presence of fluoboric acid, methyl reserpate may furnish the desired methyl 18-O-(2-dimethyl-amino)-reserpate.

A modification of the above procedure, comprises reacting a deserpidic acid of the formula shown in Fig. 5 of the drawings in which R_2, R_4, R_5, R_6, R_7, R_8' and R_8'' have the above-given meaning, with a diazo-compound, such as, for example, a lower diazo-alkane, a lower alkoxy-lower diazo-alkane or a tertiary amino-lower diazo-alkane, and isolating a deserpidate compound of the formula shown in Fig. 4 of the drawings in which R_1, R_2, R_4, R_5, R_6, R_7, R_8' and R_8'' have the above-given meaning.

This reaction may be carried out according to the previously-given procedures and is catalyzed by the necessary amount of one of the Lewis acids outlined hereinbefore. It may be advantageous to carry out the reaction in such manner that first the reactive carboxyl group in the 16-position is esterified. This may be done by adding part (one mol or an excess) of the diazo-reagent to the deserpidic acid compound, using appropriate solvents, and, after the addition of the necessary Lewis acid, giving to the reaction mixture the second part (one mol or an excess) of the diazo-reagent.

The compounds of this invention may also be prepared by treating deserpidates of the formula shown in Fig. 5 of the drawings in which R_1, R_2, R_4, R_5, R_6, R_7, R_8' and R_8'' have the previously-given meaning, and R_3' represents a reactive, esterified hydroxyl group, with an alkali metal compound of an alcohol of the formula R_3-OH, in which R_3 has the previously-given meaning.

A reactive esterified hydroxyl group is primarily a hydroxyl group esterified with a strong inorganic acid, especially a mineral acid, such as a hydrohalic acid, particularly hydrobromic or hydriodic acid. In the above-depicted starting materials, R_3' stands, therefore, advantageously for halogen, particularly for bromine or iodine.

The reactive ester group, upon treatment with an alkali metal compound of an alcohol of the formula R_3-OH, is being exchanged for an ether group, represented by the radical R_3-O-, in which R_3 has the previously-given meaning. Such alkali metal, *e.g.* lithium, sodium or potassium, compounds of alcohols, particularly of lower alkanols, lower alkoxy-lower alkanols or tertiary amino-lower alkanols, are known and may be prepared according to known procedures, for example, by reacting the alcohol with the alkali metal. The reaction of the metal reagent with the deserpidate compound may be carried out under known conditions, preferably in the presence of an inert solvent, for example, an alcohol, *e.g.* a lower alkanol, such as the alcohol used for the preparation of the alkali metal reagents described hereinabove. In this reaction, certain transesterification of the esterified carboxyl group in the 16-position of the deserpidate molecule may occurs: in the final products R_1 and R_3 may, therefore, have identical meaning.

The starting materials used in the above reaction are known, or, if new, may be prepared according to the methods used for the manufacture of the known analogs. For example, upon treating a lower alkyl deserpidate, *e.g.* methyl deserpi-

date, with a p-toluene sulfonyl halide, particularly p-toluene sulfonyl chloride, for example, in the presence of an organic base, *e.g.* pyridine, the lower alkyl, *e.g.* methyl, 18-O-(p-toluene sulfonyl)-deserpidate may be formed. The latter, when reacted with an alkali metal halide, *e.g.* lithium, sodium or potassium bromide or iodide, in the presence of an inert solvent, *e.g.* acetonitrile and the like, may be converted to the desired lower alkyl 18-desoxy-18-halogeno-deserpidate.

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Dated this 29th day of December 1960.

COMPLETE SPECIFICATION.

CIBA LIMITED, CHEMICAL MANUFACTURERS, A SWISS CORPORATION, OF 141, KLYBECKSTRASSE BASLE, SWITZERLAND.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

The present application is a division of our copending Indian Patent Application No. 72915 filed 8th August 1960, which is itself divided out of Application No. 69382 filed 19th October 1959.

This invention relates to pharmaceutical preparations containing new 17-lower alkoxy-18-hydroxy-3-epi-alloyhimbane-16-carboxylic acid esters etherified in the 18-position with an alcohol of aliphatic character and having the nucleus of formula shown in Fig. 1 of the drawings accompanying this Specification, in which the substituents in the 16-, 17- and 18-position have the same configuration as in d- or l-reserpine, and salts of these compounds, with the proviso that in the reserpic acid esters etherified in 18 position the ether radical bound to the 18-O-atom and the alcohol radical of the ester group together contain more than 2 carbon atoms. As used above and hereinafter in connection with hydrocarbon radicals the word "lower" defines such radicals as contain 1 to 7 chain-carbon atoms.

The new ethers may contain further substituents, for example aliphatic hydrocarbon radicals, etherified or esterified hydroxyl groups, etherified mercapto groups, nitro or amino groups, halogen atoms and/or halogen-lower alkyl groups. These substituents are preferably in the positions 9 to 12 of the aromatic ring A, and in the positions 5 or 6 of the heterocyclic ring C more particularly aliphatic hydrocarbon radicals.

Animal feeding stuffs containing the compounds defined in the preceding paragraphs form the subject matter of copending Indian Patent Application No. 74742.

More especially the invention relates to pharmaceutical preparations containing compounds of the formula shown in Fig. 2 of the drawings accompanying this Specification, in which R_1 stands for unsubstituted or substituted lower alkyl groups, R_2 for lower alkyl, R_3 for unsubstituted or substituted hydrocarbon radicals of aliphatic character, R_4 and R_5 each represents a hydrogen atom, a lower aliphatic hydrocarbon radical, an etherified or esterified hydroxyl group, an etherified mercapto group, a nitro or amino group, a halogen atom or a halogen-lower alkyl radical, and $R_4 + R_5$ in adjacent positions may together also form a cyclic substituent, and R_6 in one of the positions 5 or 6 stands for hydrogen or a lower alkyl radical, and salts of these compounds, with the proviso that in the reserpic acid esters etherified in the 18-position the ether radical bound to the 18-O-atom and the alcohol radical of the ester group together contain more than 2 carbon atoms.

Substituents of the lower alkyl groups R_1 are, for example, etherified hydroxyl groups or tertiary amino groups. The hydrocarbon radicals of aliphatic character represented by R_3 are, for example, lower alkyl, lower alkenyl, cycloalkyl, cycloalkenyl, cycloalkyl-lower alkyl or aryl-lower alkyl or -alkenyl; these groups may be, for example, further substituted by etherified hydroxyl or mercapto groups, amino groups, acyl radicals or halogen atoms, and the aryl radicals may in addition be substituted by lower alkyl, halogenalkyl or nitro groups.

Examples for the alcohol radical of the ester group in 16-position and the ether radical bound in 18-position to the oxygen atom, especially for the radicals R_1 and R_3 in formula shown in Fig. 2 of the drawings accompanying this specification are the following groups; lower alkyl with 1 to 7, and preferably 1 to 4, carbon atoms, such as methyl, ethyl, n- or iso-propyl, n- or iso-butyl, n- or iso-pentyl, for example neopentyl, n-hexyl or n-heptyl, etherified hydroxy-lower alkyl, primarily lower alkoxy-lower alkyl in which the lower alkoxy radical contains 1 to 4 carbon atoms and represents for example methoxy, ethoxy, n- or iso-propoxy or n-butoxy, tertiary amino-lower alkyl in which the tertiary amino group is primarily di-lower alkylamino with 2 to 8 carbon atoms, such as dimethylamino, methylethylamino, diethylamino, di-n-propylamino, di-isopropyl-amino or di-n-butylamino, or stands for alkyleneamino with preferably 4 to 6 ring carbon atoms in which the alkylene radical may also be interrupted by hetero atoms, for example pyrrolidino, piperidino, hexamethyleneimino, oxa-alkyleneamino such as morpholino, aza-alkyleneamino, such as piperazino, or 4-lower alkyl-piperazino, such as 4-methyl-piperazino.

The lower alkyl radical containing the above mentioned substituted hydroxyl or amino groups contains 2 to 7, and preferably 2 or 3, carbon atoms, and separates these groups from the ester or ether oxygen atom by at least 2 carbon atoms; it consequently represents, for example, 1 :2-ethylene, 1 :2-, 2 :3- or 1 :3-propylene, 1 :3-or 1 :4-butylene.

The substituted hydroxyl or amino-lower alkyl groups thus represent, for example, 2-lower alkoxy-ethyl, such as 2-methoxy-ethyl or 2-ethoxy-ethyl, 2- or 3-lower alkoxypropyl, such as 2-methoxy-propyl or 2-ethoxy-propyl, 3-methoxy-propyl or 3-ethoxy-propyl, 2-di-lower alkylamino ethyl, such as 2-dimethylamino-ethyl or 2-diethylamino-ethyl, 2- or 3-di lower alkylamino-propyl, such as 2-dimethylamino-propyl or 2-diethyl-amino-propyl, 3-dimethylamino-propyl or 3-diethyl-amino-propyl, 2-lower alkyleneimino-ethyl, such as 2-pyrrolidino-ethyl, 2-piperidino-ethyl, 3-lower alkyleneimino-propyl, such as 3-pyrrolidino-propyl, 3-piperidino-propyl, 2-(4-lower alkyl-piperazino)-ethyl, such as 2-(4-methyl-piperazino)-ethyl, 2-(4-ethyl-piperazino)-ethyl or 3-(4-lower alkyl-piperazino)-propyl, such as 3-(4-methyl-piperazino)-propyl or 3-(4-ethyl piperazino)-propyl.

For the radical bound in 18-position to the oxygen atom, particularly the radical R_3 in formula shown in Fig. 2 of the drawings accompanying this specification, the following unsubstituted or substituted hydrocarbon radicals of aliphatic character may be given as additional examples: lower alkenyl, preferably with 3 to 5 carbon atoms, such as allyl, 2-methallyl, butenyl-(2), 3-methyl-butenyl-(2), pentenyl-(2) cycloalkyl with 3 to 8, and preferably 5 or 6, ring carbon atoms, such as cyclopropyl, cyclopentyl, cyclohexyl, cycloheptyl or cyclo octyl, cycloalkenyl preferably with 5 or 6 ring carbon atoms, such as cyclopentenyl-(3) or cyclohexenyl-(2), cycloalkyl-lower alkyl with 3 to 8, and advantageously 5 or 6, ring carbon atoms and 1 to 4 chain carbon atoms, such as cyclopentyl-methyl, 1- or 2-cyclopentyl-ethyl, cyclohexylmethyl, 2-cyclohexyl-ethyl, araliphatic hydrocarbon radicals for example, aryl-lower alkyl, such as benzyl, diphenyl-methyl, 1- or 2-phenyl-ethyl, or aryl-lower alkenyl such as 3-phenylallyl in which the aryl radical may be substituted, or example by lower alkyl, such as methyl or ethyl, lower alkoxy, such as methoxy or ethoxy, lower alkenyl-oxy, such as allyloxy, halogen, such as chlorine or bromine, lower alkoxy-carbonyloxy, such as methoxy-carbonyloxy or ethoxy-

carbonyloxy, halogen-lower alkyl, such as trifluoromethyl, nitro or amino, for example di-lower alkylamino, such as dimethylamino; and finally lower alkyl substituted by acyl, preferably alkanoyl, such as acetyl, propionyl, carbo-lower alkoxy, such as carbomethoxy or carbethoxy, etherified mercapto, for example lower alkyl-mercapto, such as methyl-mercapto or ethyl-mercapto, or halogen, such as chlorine or bromine, for example lower alkanoyl-lower alkyl, such as acetyl-methyl or propionyl-methyl, carbo-lower alkoxy-lower alkyl, such as carbomethoxy-methyl or carbethoxy-methyl, lower alkyl-mercapto-lower alkyl, such as methylmercapto-methyl or ethylmercapto-ethyl, or halogen-lower alkyl, such as chloromethyl.

The lower alkoxy group in the 17-position, particularly the radical R_3O of formula shown in Fig. 2 of the drawings accompanying this specification, contains advantageously 1 to 4, carbon atoms and stands, for example, for ethoxy, n- or isopropoxy or n- or iso-butoxy, but especially for methoxy.

Substituents of the ring A, primarily the radicals R_4 and R_5 in formula shown in Fig. 2 of the aforesaid drawings, are, for example the following groups: lower aliphatic hydrocarbon radicals, especially lower alkyl, preferably such with 1 to 4 carbon atoms, such as methyl, ethyl, n- or iso-propyl or n- or iso-butyl, etherified hydroxyl, for example lower alkoxy, preferably such with 1 to 4 carbon atoms, such as methoxy, ethoxy, n- or iso-propoxy or n- or iso-butoxy, cyclo alkyloxy, such as cyclopentyloxy or cyclohexyloxy, cyclo-alkyl-lower alkoxy, such as cyclopentyl-methoxy, 2-cyclopentyl-ethoxy or cyclohexyl-methoxy, aryloxy, such as phenoxy, aryl-lower alkoxy, for example phenyl-lower alkoxy, such as benzyl-oxy, diphenylmethoxy or 2-phenyl-ethoxy, in which the aryl radicals may be substituted as shown above, esterified hydroxyl, for example lower alkoxy-carbonyloxy, such as methoxy or ethoxy-carbonyloxy, lower alkanoyloxy, such as acetoxy or propionyloxy, halogen, such as fluorine, chlorine, bromine or iodine, etherified mercapto, for example lower alkyl-mercapto, primarily such with 1 to 4 carbon atoms, such as methylmercapto or ethylmercapto, nitro, amino, primarily tertiary amino, for example di-lower alkylamino, such as dimethylamino, methyl-ethylamino or diethylamino, or halogen-lower alkyl, such as trifluoromethyl. When 2 adjacent substituents, for example the radicals R_4 and R_5, together form a cyclic radical, this may, for example be lower alkylenedioxy, such as methylenedioxy.

As substituents in the positions of the molecule not especially defined, particularly in those of ring C, there may be mentioned, for example aliphatic hydrocarbon radicals, especially lower alkyl, primarily such with 1 to 4 carbon atoms, particularly methyl but also ethyl, n- or iso-propyl. The radical R_6 in formula shown in Fig. 2 of the aforesaid drawings, represents primarily hydrogen. It may also represent lower alkyl, especially methyl.

Salts of the new compounds are particularly therapeutically useful addition salts, especially those of inorganic acids, for example mineral acids, such as hydrochloric acid, hydrobromic acid, sulphuric or phosphoric acids, or of organic acids, such as acetic acid, propionic acid, glycolic acid, lactic acid, pyruvic acid, oxalic acid, malonic acid, succinic acid, maleic acid, fumaric acid, malic acid, tartaric acid, citric acid, ascorbic acid, citraconic acid, hydroxymaleic acid or dihydroxymaleic acid, benzoic acid, phenylacetic acid, 4-aminobenzoic acid, 4-hydroxybenzoic acid, anthranilic acid, cinnamic acid, mandelic acid, salicylic acid, 4-aminosalicylic acid, 2-phenoxy-benzoic acid, 2-acetoxy-benzoic acid, methane-sulfonic acid, ethane-sulfonic acid, 2 hydroxy-ethane-sulphonic acid or paratoluene-sulphonic acid Mono- or poly-salts may be formed.

In view of the fact that several asymmetrical carbon atoms are present in the new compounds, the latter may be obtained as mixtures of racemates, pure racemates or as optical antipodes.

The new preparations have sedative and tranquillising properties and also an antihypertensive effect. They are distinguished particularly by the fact that in contrast to preparations containing the natural alkaloids which show a slow onset of the pharmacological action and an often undesirably long-lasting effect, the onset of their effect is much more rapid and of definite duration, i.e. medication is more easily controlled.

Accordingly, the new pharmaceutical preparations can, therefore,, be used as medicaments in human or veterinary medicine. They may, for example, be used as sedatives or tranquillizers for the treatment of hyperactivity, tension and agitation and in human medicine also as anti hypertensive agents for the treatment of high blood pressure, for example, benign or maligant hypertension, renal hypertension or hypertension associated with pregnancy, such as toxaemia of pregnancy.

Especially valuable preparations are those which contain compounds of formula shown in Fig. 3 of the drawings accompanying this specification, in which R_1 and R_3 each stand for lower alkyl, primarily containing 1 to 4 carbon atoms, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, secondary butyl, and R_x for lower alkoxy containing 1 to 4 carbon atoms, especially methoxy, but also ethoxy, n-propoxy, isopropoxy or n-butoxy, R_x being especially in one of the positions 10 or 11, and the salts of these compounds, with the proviso that in the reserpic acid esters etherified in 18-position the ether radical bound to the 18-O-atom and the alcohol radical of the ester group together contain more than 2 carbon atoms. These compounds are preferably in the form of that antipode which corresponds to the laevorotatory methyl reserpate.

Examples of especially effective compounds may be seen in the Table below; the substituents refer to formula shown in Fig. 2 of the aforesaid drawings.

R_1	R_2	R_3	R_4
CH_3	CH_3	C_2H_5	CH_3O
CH_3	CH_3	n-C_3H_7	CH_3O
CH_3	CH_3	i-C_3H_7	CH_3O
CH_3	CH_3	n-C_4H_9	CH_3O
CH_3	CH_3	i-C_4H_9	CH_3O
C_2H_5	CH_3	CH_3	CH_3O
C_2H_5	CH_3	C_2H_5	CH_3O
C_2H_5	CH_3	n-C_3H_7	CH_3O
C_2H_5	CH_3	n-C_4H_9	CH_3O
n-C_3H_7	CH_3	CH_3	CH_3O
n-C_3H_7	CH_3	C_2H_5	CH_3O
i-C_3H_7	CH_3	CH_3	CH_3O
i-C_3H_7	CH_3	n-C_3H_7	CH_3O
n-C_4H_9	CH_3	CH_3	CH_3O
n-C_4H_9	CH_3	C_2H_5	CH_3O
i-C_4H_9	CH_3	CH_3	CH_3O
n-C_5H_{11}	CH_3	CH_3	CH_3O
n-C_6H_{13}	CH_3	CH_3	CH_3O
CH_3	CH_3	CH_3	H
CH_3	CH_3	C_2H_5	H
CH_3	CH_3	n-C_3H_7	H
CH_3	CH_3	i-C_3H_7	H
CH_3	CH_3	n-C_4H_9	H
CH_3	CH_3	sec.-C_4H_9	H
C_2H_5	CH_3	CH_3	H
C_2H_5	CH_3	C_2H_5	H
C_2H_5	CH_3	n-C_3H_7	H
n-C_3H_7	CH_3	CH_3	H
n-C_3H_7	CH_3	C_2H_5	H
i-C_3H_7	CH_3	CH_3	H
i-C_3H_7	CH_3	n-C_3H_7	H
n-C_4H_9	CH_3	CH_3	H
sec.-C_4H_9	CH_3	CH_3	H
n-C_5H_{11}	CH_3	CH_3	H

Other endproducts which illustrate the subject matter of the invention are, for example, those of formula shown in Fig. 4 of the drawings accompanying this specification, in which R_1 to R_9 have the following meanings:

R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9
CH_3	CH_3	CH_3	H	H	CH_3O	H	H	H
CH_3	CH_3	C_2H_5	H	H	CH_3O	H	H	H
CH_3	CH_3	n-C_3H_7	H	H	CH_3O	H	H	H
C_2H_5	CH_3	CH_3	H	H	CH_3O	H	H	H
CH_3	CH_3	CH_3	H	CH_3O	H	H	H	H
CH_3	CH_3	C_2H_5	H	CH_3O	H	H	H	H
CH_3	CH_3	n-C_3H_7	H	CH_3O	H	H	H	H
C_2H_5	CH_3	CH_3	H	CH_3O	H	H	H	H
n-C_3H_7	CH_3	CH_3	H	CH_3O	H	H	H	H
i-C_3H_7	CH_3	CH_3	H	CH_3O	H	H	H	H
CH_3	CH_3	CH_3	C_2H_5O	H	H	H	H	H
CH_3	CH_3	C_2H_5	C_2H_5O	H	H	H	H	H
CH_3	CH_3	CH_3	n-C_3H_7O	H	H	H	H	H
CH_3	CH_3	C_2H_5	n-C_3H_7O	H	H	H	H	H
CH_3	CH_3	CH_3	i-C_3H_7O	H	H	H	H	H
C_2H_5	CH_3	CH_3	i-C_3H_7O	H	H	H	H	H
CH_3	CH_3	CH_3	n-C_4H_9O	H	H	H	H	H
CH_3	CH_3	C_2H_5	n-C_4H_9O	H	H	H	H	H
CH_3	CH_3	CH_3	H	H	H	CH_3O	H	H
C_2H_5	CH_3	CH_3	H	H	H	CH_3O	H	H
CH_3	CH_3	CH_3	CH_3O	H	H	H	H	CH_3
CH_3	CH_3	C_2H_5	CH_3O	H	H	H	H	CH_3
C_2H_5	CH_3	CH_3	CH_3O	H	H	H	H	CH_3
CH_3	CH_3	CH_3	CH_3O	H	H	H	CH_3	H
CH_3	CH_3	n-C_4H_9	CH_3O	H	H	H	CH_3	H
C_2H_5	CH_3	CH_3	CH_3O	H	H	H	CH_3	H
CH_3	CH_3	CH_3	H	H	H	H	CH_3	H
CH_3	CH_3	n-C_3H_7	H	H	H	H	CH_3	H
C_2H_5	CH_3	CH_3	H	H	H	H	CH_3	H
CH_3	CH_3	CH_3	H	H	CH_3	H	H	H
CH_3	CH_3	C_2H_5	H	H	CH_3	H	H	H
n-C_3H_7	CH_3	CH_3	H	H	CH_3	H	H	H
CH_3	CH_3	CH_3	CH_3	H	H	H	H	H
C_2H_5	CH_3	CH_3	CH_3	H	H	H	H	H
C_2H_5	CH_3	n-C_4H_9	CH_3	H	H	H	H	H
CH_3	CH_3	CH_3	CH_3O	CH_3O	H	H	H	H
CH_3	CH_3	C_2H_5	CH_3O	CH_3O	H	H	H	H
C_2H_5	CH_3	n-C_3H_7	CH_3O	CH_3O	H	H	H	H
CH_3	CH_3	CH_3	O-CH_2-O		H	H	H	H
C_2H_5	CH_3	CH_3	O-CH_2-O		H	H	H	H
CH_3	CH_3	CH_3	H	$C_6H_5CH_2O$	H	H	H	H
CH_3	CH_3	C_2H_5	H	$C_6H_5CH_2O$	H	H	H	H
C_2H_5	CH_3	CH_3	H	$C_6H_5CH_2O$	H	H	H	H
CH_3	CH_3	CH_3	$C_6H_5CH_2O$	H	H	H	H	H
CH_3	CH_3	C_2H_5	$C_6H_5CH_2O$	H	H	H	H	H
C_2H_5	CH_3	CH_3	$C_6H_5CH_2O$	H	H	H	H	H
CH_3	CH_3	CH_3	CH_3S	H	H	H	H	H
CH_3	CH_3	C_2H_5	CH_3S	H	H	H	H	H
C_2H_5	CH_3	CH_3	CH_3S	H	H	H	H	H
CH_3	CH_3	CH_3	C_2H_5S	H	H	H	H	H
C_2H_5	CH_3	C_2H_5	C_2H_5S	H	H	H	H	H
n-C_3H_7	CH_3	CH_3	C_2H_5S	H	H	H	H	H
CH_3	CH_3	CH_3	H	Cl	H	H	H	H
CH_3	CH_3	C_2H_5	H	Cl	H	H	H	H
C_2H_5	CH_3	n-C_3H_7	H	Cl	H	H	H	H
CH_3	CH_3	CH_3	CH_3O	Br	H	H	H	H
CH_3	CH_3	C_2H_5	CH_3O	Br	H	H	H	H
C_2H_5	CH_3	C_2H_5	CH_3O	Br	H	H	H	H
CH_3	C_2H_5	CH_3	CH_3O	H	H	H	H	H
CH_3	C_2H_5	C_2H_5	CH_3O	H	H	H	H	H
CH_3	n-C_3H_7	CH_3	CH_3O	H	H	H	H	H
C_2H_5	n-C_3H_7	CH_3	CH_3O	H	H	H	H	H
CH_3	i-C_3H_7	CH_3	CH_3O	H	H	H	H	H
CH_3	i-C_3H_7	C_2H_5	CH_3O	H	H	H	H	H
CH_3	C_2H_5	CH_3	H	H	H	H	H	H
CH_3	C_2H_5	C_2H_5	H	H	H	H	H	H
C_2H_5	C_2H_5	C_2H_5	H	H	H	H	H	H
$CH_3OC_2H_4$	CH_3	CH_3	CH_3O	H	H	H	H	H

R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9
$CH_3OC_2H_4$	CH_3	C_2H_5	CH_3O	H	H	H	H	H
$C_2H_5OC_2H_4$	CH_3	CH_3	CH_3O	H	H	H	H	H
-"-	CH_3	n-C_3H_7	CH_3O	H	H	H	H	H
CH_3 | CH_3OCHCH_2	CH_3	CH_3	CH_3O	H	H	H	H	H
$CH_3OC_2H_4$	CH_3	CH_3	CH_3O	H	H	H	H	H
$CH_3OC_2H_4$	CH_3	CH_3	H	H	H	H	H	H
$CH_3OC_2H_4$	CH_3	C_2H_5	H	H	H	H	H	H
$C_2H_5OC_2H_4$	CH_3	CH_3	H	H	H	H	H	H
$(CH_3)_2N$-C_2H_5	CH_3	CH_3	CH_3O	H	H	H	H	H
-"-	CH_3	C_2H_5	CH_3O	H	H	H	H	H
$(C_2H_5)_2NC_2H_4$	CH_3	CH_3	CH_3O	H	H	H	H	H
$(CH_3)_2NC_2H_4$	CH_3	CH_3	CH_3O	H	H	H	H	H
$(CH_3)_2NC_2H_4$	CH_3	CH_3	H	H	H	H	H	H
$(CH_3)_2NC_2H_4$	CH_3	C_2H_5	H	H	H	H	H	H
$(CH_3)_2NCHCH_2$ | CH_3	CH_3	CH_3	H	H	H	H	H	H
i-C_5H_{11}	CH_3	CH_3	CH_3O	H	H	H	H	H
n-$C_4H_9OC_2H_4$	CH_3	CH_3	CH_3O	H	H	H	H	H
i-$C_4H_9OC_2H_4$	CH_3	CH_3	CH_3O	H	H	H	H	H
$CH_3OC_2H_4$	CH_3	n-C_3H_7	CH_3O	H	H	H	H	H
CH_3	CH_3	CH_3	H	H	H	H	H	CH_3
CH_3	CH_3	n-C_3H_7	H	H	H	H	H	CH_3
C_2H_5	CH_3	CH_3	H	H	H	H	H	CH_3
CH_3	CH_3	C_2H_5	CH_3O	H	H	H	CH_3	H
n-C_3H_7	CH_3	CH_3	CH_3O	H	H	H	CH_3	H
CH_3	CH_3	n-C_4H_9	H	H	CH_3	H	H	H
CH_3	CH_3	n-C_3H_7	CH_3	H	H	H	H	H
n-C_3H_7	CH_3	CH_3	CH_3	H	H	H	H	H
C_2H_5	CH_3	CH_3	CH_3O	CH_3O	H	H	H	H
CH_3	CH_3	n-C_4H_9	H	H	H	CH_3O	H	H
n-C_3H_7	CH_3	CH_3	H	H	H	CH_3O	H	H
C_2H_5	CH_3	CH_3	CH_3O	H	H	H	H	H
CH_3	CH_3	n-C_3H_7	n-C_3H_7O	H	H	H	H	H
C_2H_5	CH_3	CH_3	n-C_3H_7O	H	H	H	H	H
C_2H_5	CH_3	CH_3	n-C_3H_7O	H	H	H	H	H
CH_3	CH_3	C_2H_5	O-CH_2-O		H	H	H	H
n-C_3H_7	CH_3	CH_3	H	$C_6H_5CH_2O$	H	H	H	H
n-C_3H_7	CH_3	CH_3	CH_3S	H	H	H	H	H
CH_3	CH_3	n-C_3H_7	C_2H_5S	H	H	H	H	H
CH_3	CH_3	n-C_3H_7	H	Cl	H	H	H	H
i-C_3H_7	CH_3	CH_3	H	Cl	H	H	H	H
CH_3	CH_3	n-C_4H_9	CH_3O	Br	H	H	H	H
C_2H_5	CH_3	CH_3	CH_3O	Br	H	H	H	H
CH_3	C_2H_5	n-C_3H_7	CH_3O	H	H	H	H	H
n-C_3H_7	C_2H_5	CH_3	CH_3O	H	H	H	H	H
CH_3	n-C_3H_7	C_2H_5	CH_3O	H	H	H	H	H
C_2H_5	i-C_3H_7	C_2H_5	CH_3O	H	H	H	H	H
CH_3	C_2H_5	i-C_4H_9	H	H	H	H	H	H
C_2H_5	C_2H_5	CH_3	H	H	H	H	H	H

The new preparations can be prepared by conventional methods from the above mentioned 17-lower alkoxy-18-hydroxy-3-epi-alloyohimbane-16-carboxylic acid esters etherified in the 18-position, or the salts of these compounds. These preparations contain the active substance in admixture with a pharmaceutical organic or inorganic, solid or liquid excipient suitable for enteral, for example oral, or parenteral administration. For making up the preparations such substances may be used as do not react with the new compounds, such as, for example, water, gelatine, lactose, starches, magnesium stearate, talc, vegetable oils, benzyl alcohols gums, polyalkylene glycols, white petroleum jelly, cholesterol or any other known excipient. The pharmaceutical preparations may be in the form, for example, of tablets, dragees or capsules or in liquid form as solutions, suspensions or emulsions. They may be sterilized and/or contain auxiliary substances, such as preserving, stabilizing, wetting or emulsifying agents, salts for varying the osmotic pressure or buffers. They may also contain other therapeutically useful substances, for example hypotensive agents.

The new pharmaceutical preparations contain from about 0.05 to about 75%, advantageously 0.05 to 50% of the active substance. Especially useful are compositions, such as injectable solutions or preparations for oral use, containing 0.05 to 10% of the active substance. For example preparations for oral use, such as tablets, preferably contain from 0.1 to 5% of the active ingredient.

The 17-lower alkoxy-18-hydroxy-3-epi-alloyohimbane-16-carboxylic acid esters etherified in the 18-position, and the salts of these compounds, used in the manufacture of the new preparations are obtained according to the process of Indian Specification No. 72915. Said process consists in reacting a 17-lower alkoxy-18-hydroxy-3-epi-alloyohimbane-16-carboxylic acid ester with the nucleus of formula shown in Fig. 1 of the drawings accompanying this specification, in which the substituents in the 16-, 17- and 18-position have the same configuration as in d- or ℓ-reserpine, especially a compound of formula shown in Fig. 5 of the drawings accompanying this specification, in which R_1, R_2 and R_4 to R_9 have the meanings defined for formula shown in Fig. 2 of the

aforesaid drawings, or a salt of these compounds, with a diazo compound of aliphatic character, preferably one of an unsubstituted or substituted hydrocarbon of aliphatic character, in the presence of a strong inorganic Lewis acid and, if desired, converting a resulting base into a salt or converting a resulting salt into a free compound.

18-O-methyl-reserpic acid methyl ester and its salts as well as a process for preparing same form the subject matter of copending Indian Patent Application No. 69382.

Pharmaceutical preparations containing the 18-O-methyl-reserpic acid methyl ester or physiologically tolerable acid addition salts thereof form the subject matter of copending Indian Patent Application No. 74722. Animal feeding stuffs containing the latter compounds are the subject matter of copending Indian Patent Application No. 74735.

The following Examples illustrate the invention.

Example 1.

Therapeutically acceptable tablets containing 0.00025 g. of the active substance (procedure for 10,000 tablets):

Ingredients:

methyl 18-O-ethyl-reserpate	2·500 g.
Lactose Spray Dried	942·500 g.
Corn Starch	50·000 g.
Magnesium Stearate	5·000 g.

The methyl 18-O-ethyl-reserpate is triturated with the corn starch and the mixture is forced through a No. 60 screen. The lactose and the magnesium stearate is passed through a No. 20 screen, and all ingredients are mixed in a suitable mixer until the mix is homogenous. Tablets weighing 0.1 g. are compressed using 0.25 inch punches and dies.

The methyl 18-O-ethyl-reserpate used as the active ingredient can be obtained as follows:

To a solution of 2.48 g. of methyl reserpate in 400 ml. of methylene chloride, maintained at -10 to -15°, is added 66 ml. of a fluoboric acid solution while stirring. (The latter is prepared as follows: Commercially available fifty per cent. aqueous fluoboric acid is concentrated by partial evaporation under reduced pressure to an approximately 14 N solution, determined by titration with a standard sodium hydroxide solution. A stock solution of approximately 0.1 N strength is prepared by dissolving 1 ml. of the concentrated fluoboric acid in a mixture of 110 ml. of absolute ether and 30 ml. of methylene chloride). A small precipitate forms during the addition, which represents, probably, a salt of methyl reserpate with the acid.

113 ml of a 0.212 molar solution of diazoethane in methylene chloride is added to the stirred reaction mixture over a period of about ten minutes, whereby the temperature is maintained at -10°. The previously mentioned precipitate dissolved again. An additional 1 ml. of the stock solution of fluoboric acid is given to the reaction mixture, and the solution is stirred for a few more minutes. 2 ml. of glacial acetic acid is added with the intent to destroy any excess of diazoethane.

The solution is washed twice with five per cent aqueous sodium carbonate and once with saturated aqueous sodium chloride, the organic layer is dried over anhydrous sodium sulfate and evaporated under reduced pressure, whereupon a tan, solid material can be recovered. The product may be purified as follows: As much as possible of the residue is dissolved in 50-60 ml. of benzene at room temperature; the undissolved material is filtered off. The filtrate is chromatographed on about 40 g. of aluminum oxide (Woelm, neutral, activity I); the desired methyl 18-O-ethyl-reserpate is eluted with benzene, containing 0.2 per cent of methanol. The oily, yellow solid is washed with cold ether and recrystallized from a 1:3-mixture of benzene and cyclo-hexane, using charcoal as a decolorizing agent, m.p. 221-22,5° (with decomposition).

The purification step may also be carried out as follows: 7.5 g. of benzene-soluble material, obtained from the tan, solid product, is dissolved in 100 ml. of benzene and placed on a column containing 240 g. of aluminium oxide (Woelm, neutral activity II-III). The column is washed with about 600 ml. of benzene, and subsequently with about 3,000 ml. of methylene chloride and about 2,000 ml. of methylene chloride containing 0.5 per cent of methanol. The fractions obtained with methylene chloride and the first fractions eluted with methylene chloride and the first fractions eluted with the methylene chloride-methanol mixture are combined after evaporation of the solvent and the residue is recrystallized using a 1:3-mixture of benzene and cyclohexane and charcoal as an adsorbent. The resulting pure methyl 18-O-ethyl-reserpate is identical with the above-described product.

Example 2.

Tablets containing 0.0005 g. of ethyl 18-O-methyl-reserpate are prepared as follows (procedure for 10,000 tablets):

Ingredients:

ethyl 18-O-methyl-reserpate	5·000 g.
Lactose	1420·000 g.
Tragacanth 550	15·000 g.
Polyethylene Glycol 6000	30·000 g.
Talc	22·500 g.
Magnesium Stearate	7·500 g.
Alcohol 50%	q.s.

The ethyl 18-O-methyl-reserpate is triturated with the tragacanth and forced through a No. 60 screen. The lactose, the talc and the magnesium stearate are forced through a No. 20 screen, and all ingredients are mixed until homogenous. The polyethylene glycol is dissolved in 40 ml. of the alcohol, and the above-mixed powder is wetted with this solution, if necessary by adding an additional amount of alcohol. The moist mass is passed through a No. 10 screen and dried at about 37°. The resulting granules are broken on a No. 16 screen. Tablets weighing 0.150 g. are compressed using 9/32 inch dies and standard concave punches, uppers bisected. The ethyl 18-O-methyl-reserpate used as the active ingredient can be obtained in an analogous manner as shown for methyl 18-O-ethyl-reserpate in Example 1.

We claim:

1. Pharmaceutical preparations containing 0.005 to 75% of 17-lower alkoxy-18-hydroxyl-3-epi-alloyohimbane-16-carboxylic acid esters etherified in the 18-position with an alcohol of aliphatic character and having the nucleus of formula shown in Fig. 1 of the drawings accompanying this specification, in which the substituents in the 16-, 17- and 18-position have the same configuration as in d- or l- reserpine, or salts of these compounds, with the proviso that in the reserpic acid esters etherified in 18-position the ether radical bound to the 18-O-atom and the alcohol radical of the ester group together contain more than 2 carbon atoms in admixture with a pharmaceutical carrier such as herein described.

2. Pharmaceutical preparations containing the new active substances mentioned in Claim 1 in admixture with a pharmaceutical solid carrier such as herein described.

3. Pharmaceutical preparations containing 0.005 to 75% of the new active substances mentioned in Claim 1 in admixture with a pharmaceutical liquid carrier such as herein described.

4. Pharmaceutical preparations for injection containing 0.005 to 75% of the new active substances mentioned in Claim 1 in admixture with a pharmaceutical carrier such as herein described.

5. Pharmaceutical preparations in tablet form containing the new active substances mentioned in Claim 1 in admixture with a pharmaceutical solid carrier such as herein described.

6. Pharmaceutical preparations in capsule form containing the new active substances mentioned in Claim 1 in admixture with a pharmaceutical solid carrier such as herein described.

7. Pharmaceutical preparations as claimed in Claims 2, 5 and 6 said preparations containing 0.005 to 75% of the active substance.

8. Pharmaceutical preparations as claimed in Claims 2 to 6 said preparations containing 0.05 to 50% of the active substance.

9. Pharmaceutical preparations as claimed in Claims 2 to 6 said preparations containing 0.05 to 10% of the active substance.

10. Pharmaceutical preparations as claimed in Claims 2, 3 and 4 said preparations containing 0.05 to 5% of the active substance.

11. Pharmaceutical preparations as claimed in Claims 1, 2, 5 and 6, said preparations containing 0.1 to 5% of the active substance.

12. Pharmaceutical preparations as claimed in Claims 1, 2, 5, 6 and 11, said preparations containing 0.25% of the active substance.

13. Pharmaceutical preparations as claimed in Claims 1, 2, 5, 6 and 11, said preparations containing 0.5% of the active substance.

B. DEPENNING,
OF DEPENNING & DEPENNING,
Agents for the Applicants.

Dated this 29th day of December 1960.

MGIP Santh.—SL—69 Patent/61—28-6-62—100.

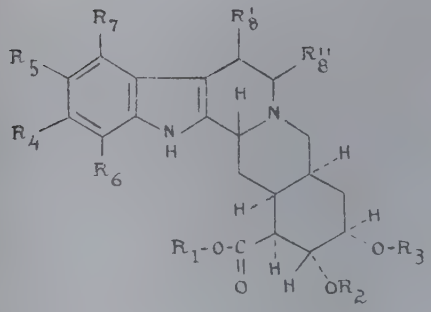

FIG 1

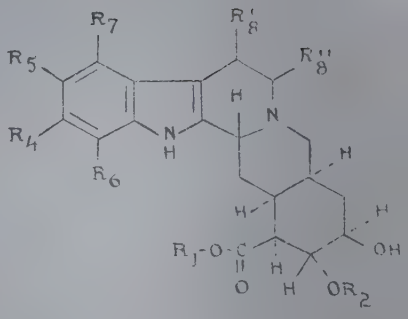

FIG. 2

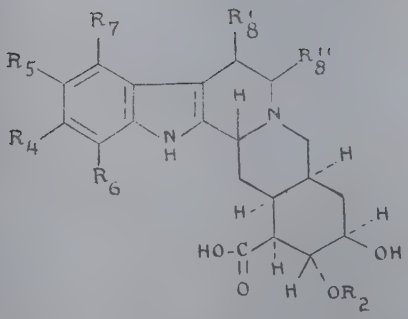

FIG. 3

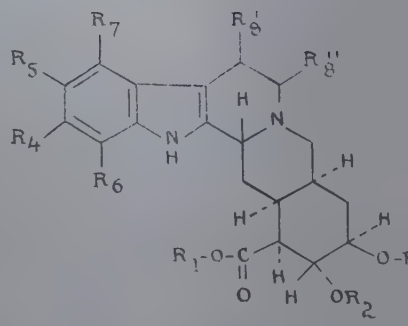

FIG. 4

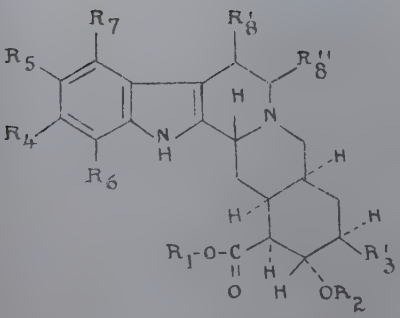

FIG. 5

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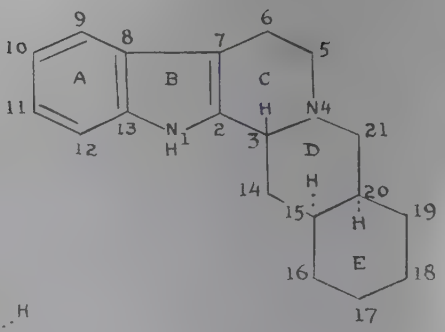

FIG.1

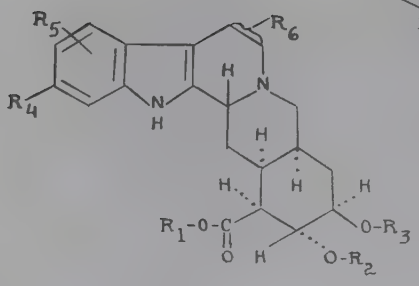

FIG.2

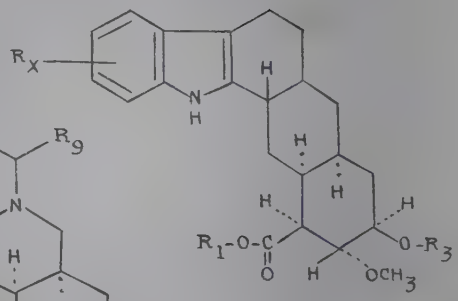

FIG.3

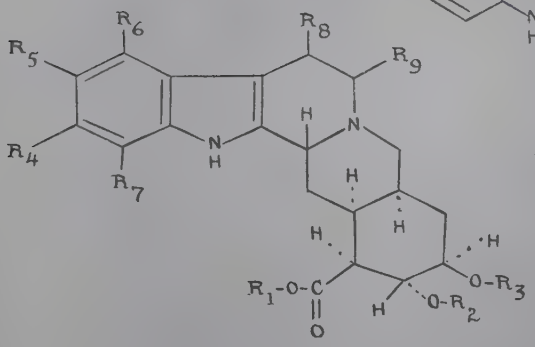

FIG.4

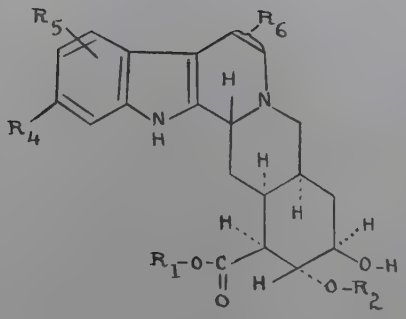

FIG.5

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GOVERNMENT OF INDIA . THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17

Specification No. 74739, filed 30th December 1960./9 Paus, 1882 (Saka).

[Open to public inspection under Section 78A (3) of the Indian Patents and Designs Act, 1911, since 1st July 1961]. (Accepted 1st October 1962).

"PESTICIDAL COMPOSITIONS CONTAINING ALPHA-SUBSTITUTED BENZALDOXIMES."

"SHELL" RESEARCH LIMITED, OF SHELL CENTRE, LONDON S.E.1, ENGLAND, FORMERLY OF ST. HELEN'S COURT, GREAT ST. HELEN'S, LONDON W.C.2., ENGLAND, A COMPANY ORGANIZED UNDER THE LAWS OF GREAT BRITAIN, A BRITISH RESEARCH COMPANY.

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This invention relates to compositions containing novel α-substituted benzaldoximes as the active ingredient. These compounds have excellent pesticidal properties. Some have excellent fungicidal properties, some have excellent herbicidal, particularly seedicidal properties and some show high toxicity to snails. The invention therefore relates to the use of said compounds as pesticides, particularly fungicides, herbicides and molluscicides.

According to the invention there is provided a pesticidal composition comprising as active ingredient one or more alpha-substituted benzaldoximes of the general formula shown in Fig. 1 of the accompanying drawings and salts thereof,

wherein X represents a halogen atom;

W represents a halogen atom or an alyl group;

n is 1, 2, 3 or 4;

Y represents a halogen atom or a hydroxy, hydrocarbyloxy, cyano thiocyano, or nitro group or a group of formula -COOR′ or $-SO_2R'$ wherein R′ represents a hydrogen atom or a hydrocarbyl group; or Y represents a group of formula $-NR^1R^2$ wherein R^1 and R^2 may be the same or different, each representing a hydrogen atom, a hydrocarbyl group, a hydrocarbyl group substituted by halogen or hydroxyl or a hydrocarbyl group substituted by halogen and hydroxyl, or R^1 represents a hydrogen atom or a hydrocarbyl group and R^2 represents a hydroxyl group of the group $-NR^3R^4$ wherein R^3 and R^4 may be the same or different, each representing a hydrogen atom or a hydrocarbyl group; or Y represents a group of formula $-NR^5.CO.NR^6R^7$ or $-NR^5.CS.NR^6R^7$, or a tautomeric form thereof, wherein R^5, R^6 and R^7 may be same or different, each representing a hydrogen atom or a hydrocarbyl group; or Y represents a group of formula $-SR^8$ or $-SO_xR^9$ wherein *x* is 1 or 2 and R^8 represents a hydrogen atom or R^8 and R^9 each represent a hydrocarbyl group, or a hydrocarbyl group substituted by halogen, Z represents a hydrogen atom, and acyl group or an alkoxylcarbonyl group, in admixture with a solid carrier as hereinbefore defined and/or a surface active agent, or in admixture with a liquid carrier and a surface active agent.

The α-substituted benzaldoximes of the general formula shown in Fig. 1 as defined above can exist as *syn-* or *anti*-isomers or as mixtures thereof and the present invention relates to any or all of these forms.

In the above formula, the halogen is preferably chlorine or bromine, but fluorine and iodine are also possible as nuclear substituents. Where two or more halogen atoms are present in the molecule, the atoms may be of the same or different halogens. In general, the activity of herbicidal compounds is favoured by the presence of 2:6-dihalo substituents, while in the fungicidally active α-cyano benzaldoximes, the 2:4-dihalo derivatives are at least as active as the 2:6-dihalo derivatives.

The term hydrocarbyl used herein means a hydrocarbon group and the term "hydrocarbyloxy" means a group OR″ in which R″ represents a hydrocarbyl group. The hydrocarbyl group may be a saturated or unsaturated aliphatic or cycloaliphatic hydrocarbon group or an aromatic hydrocarbon group, preferably a phenyl group.

In the general formula shown in Fig. 1, Y may represent a hydrocarbyloxy group. This is preferably an alkoxy group of 1 to 4 carbon atoms.

When R′ in the group -COOR′ or $-SO_2R'$ represents a hydrocarbyl group, this is preferably an alkyl group of 1 to 4 carbon atoms.

The hydrocarbyl or substituted hydrocarbyl groups which R^1 or R^2, or R^1 and R^2 in the group $-NR^1R^2$ may represent, are preferably saturated or unsaturated aliphatic hydrocarbon groups of 1 to 4 carbon atoms which may be unsubstituted or substituted by hydroxyl, or halogen, preferably chlorine.

Y may also represent the group $-NR^1OH$, R^1 preferably representing a hydrogen atom or an aryl group, especially a phenyl group. Y may also represent the group $-NR^1.NR^3R^4$. Here R^1 is preferably a hydrogen atom but may be a hydrocarbyl group, for example, an alkyl group of 1 to 4 carbon atoms. Preferably R^3 and R^4 each represent a hydrogen atom or R^3 represents a hydrogen atom and R^4 represents a phenyl group.

In the ureido and thioureido groups $-NR^5.CO.NR^6R^7$ and $-NR^5.CS.NR^6R^7$, R^5, R^6 and R^7 preferably each represent a hydoogen atom or one or more of R^5. R^6 and R^7 may represent an alkyl group of 1 to 4 carbon atoms or one may represent a phenyl or chlorinated phenyl group. Tautomeric forms of the ureido group are those shown in Fig. 2.

Tautomeric forms of the thioureido group are similar.

Examples of the above nitogen containing groups are :—

$-NH_2$, $-NHCH_3$, $N(CH_3)_2$ and its homologues; $-NH.CH_2.CH=CH_2$, $-NH.CH_2.CH(CH_3)_2$, $-NH.OH_2.CH_2OH$, $-N(CH_2.CH_2OH)_2$, -NH.CHOH.CCl_3, NH.CHOH.CBr_3, -NHCH, $-NH.NH_2$, -NH.NH-phenyl, -NH.CO.NH_2, -NH.CO.-HCH_3, -NH.CO.N$(CH_3)_2$, -NH.C(OH):NCH_3, -NH.C(OCH_3):NCH_3, -NH.CO.NH-phenyl and the thio analogues thereof. When in the group $-NR^1R^2$, R^1 and R^2 together with the nitrogen atom complete a heterocyclic ring, this ring may contain one or more hereto atoms, for example, piperidyl, morpholinyl, thiazolyl or thiazolinyl groups.

The hydrocarbyl groups which R^8 and R^9 may represent may suitably be phenyl groups or phenyl groups substituted by alkyl, preferably methyl, or by halogen, preferably chlorine. R^8 and R^9 may also represent alkyl groups, preferably of 1 to 4 carbon atoms.

Compounds of the invention in which Y represents a nitrogen containing group as specified above may be either in the form of the free base or preferably in the form of a salt with an acid. The acid used may be a mineral acid or an organic acid.

Compounds of the invention containing one or more acidic groups, for example compounds in which Y represents a carboxylic or sulphonic acid group, or a thiol group, or in which Z represents the group =NCH, may be in the form of the free

acid or of a salt. The salt may be an alkali or alkaline earth metal, especially sodium, potassium or calcium salt, an ammonium or substituted ammonium salt, for example, a triethylammonium or an alkanolammonium, especially a triethanolammonium salt.

In compounds of the general formula shown in Fig. 1 in which Z represents an acyl group, the acyl group may, for example, be the radical of an aliphatic or aromatic carboxylic, sulphonic, phosphoric or phosphonic acid. The acyl group may be substituted or may be substituted by halogen, preferably chlorine. Preferably, the acyl group is the radical of an aliphatic or chlorinated aliphatic carboxylic acid of 1 to 4 carbon atoms, for example, are acetyl or mono-, di- or trichloro-acetyl group. Where Z represents an alkoxycarbonyl group, it suitably contains 2 to 4 carbon atoms.

Compounds of the general formula shown in Fig. 1 in which Y represents a halogen atom particularly chlorine, may be prepared by introducing the dry halogen into a solution of the corresponding nuclear substituted aldoxime in an inert solvent, for example, chloroform or carbon tetrachloride. It is advantageous to carry out the halogenation in presence of a neutralising agent, for example, precipitated calcium, barium or magnesium carbonate, in order to suppress undesirable side reactions.

The α-halogen atom of the α-halobenzaldoxime can be replaced by the radical of another acid by reacting it with a salt of said acid, preferably an alkali metal salt, especially a sodium or potassium salt thereof. Thus, the α-halobenzaldoxime may be reacted with an alkali metal cyanide, thiocyanate, mercaptide, alkoxide, or sulphinate to give the corresponding α-cyano, α-thiocyano, α-mercapto, α-alkoxy or α-hydrocarbyl-sulphonyl benzaldoximes. The reaction is preferably carried out in an alcoholic solvent, for example, methanol or ethanol. The α-hydroxy compound can be prepared by reacting the α-halo-benzaldoxime with an alkali metal hydroxide in an aqueous or alcoholic solvent. Similarly, by reacting the α-halobenzaldoxime with a compound HNR^1R^2 where R^1 and R^2 have the aforesaid meanings, the corresponding α-amino and α-substituted aminobenzaldoximes can be prepared. The α-amino and α-substituted-aminobenzaldoximes may also be prepared by reacting the corresponding benzonitrile oxides with the compound HNR^1R^2. The reaction may be expressed by the equation:— $R.CN{\rightarrow}O + HNR^1R^2 \rightarrow R.C(NR^1R^2){=}NOH$ wherein R represents a benzene nucleus substituted as hereinbefore specified. The α-aminobenzaldoximes may also be prepared by addition of hydroxylamine to the nitrile group of the corresponding substituted benzonitrile. An aqueous alcoholic reaction medium may be used. The reactions are preferably carried out under anhydrous conditions in a solvent, for example, absolute alcohol or dry ether.

Ureido and thioureido derivatives may be prepared by isomerising the cyanic and thiocyanic acid salts of primary or secondary α-aminobenzaldoximes of the invention. Substituted ureido and thioureido derivatives may be prepared by reacting a primary or secondary α-aminobenzaldoxime of the invention with an ester of isocyanic or isothiocyanic acid, for example, the phenyl ester.

By reacting the α-aminobenzaldoxime with chloral or bromal, the α-(2-trihalo-1-hydroxyethylamino) derivatives can be prepared.

The α-cyanobenzaldoximes may also be prepared by reacting the corresponding benzyl cyanide with nitrous acid. The α-nitrobenzaldoximes may be prepared by reacting the corresponding aldoximes with concentrated nitric acid, preferably in an inert solvent, for example glacial acetic acid, the temperature preferably being maintained below about 15°C. The product is contaminated with the nitrile oxide formed by decomposition of the nitrolic acid. The nitrolic acid can be isolated by extracting a solution of the nitration product in a solvent, for example methylene dichloride, with aqueous ammonia and then carefully acidifying the ammonia solution, for example, with hydrochloric, sulphuric or oxalic acid. Alternatively, a solution of the nitration product in a water-soluble solvent, for example, glacial acetic acid, can be progressively diluted with water, the nitrile-oxide precipitating first, followed on further dilution by the nitrolic acid as a yellow solid. It can be purified by conversion to the ammonium salt and re-acidification as described above.

Compounds of the general formula shown in Fig. 1 in which Z represents an acyl group can be prepared by reacting the aldoxime with an acylating agent such as an acid anhydride or acid chloride or ester of a volatile alcohol according to methods well-known in the art. Since acid chlorides such as acetyl chloride are powerful dehydrating agents, however, it is necessary to work under very mild conditions when using these reagents to avoid converting the oxime to the nitrile. Mild reaction conditions should also be employed when acid anhydrides such as acetic anhydride are used.

Compounds of the general formula shown in Fig. 1 in which Z represents an alkoxycarbonyl group can be prepared by reacting an alkyl chloroformate with the aldoxime in presence of a hydrogen chloride acceptor, for example, a tertiary base, or with a salt, preferably an alkali metal salt of the oxime.

Salts of benzaldoximes of the above general formula having a basic substituent in the α-position may be prepared by reacting the base with an inorganic or organic acid preferably in a solvent, for example ether, and preferebly under anhydrous conditions. By reaction in an aqueous medium, aqueous solutions of the salts can be obtained.

The following Examples illustrate the process of the invention. In these Examples, parts by weight and parts by volume bear the same relation as the kilogram and the litre.

EXAMPLE I Preparation of α,2,4-trichlorobenzaldoxime [Fig. 3].

To a stirred suspension of 2,4-dichlorobenzaldoxime (19 w) in dry chloroform (200 v) was added a solution of chlorine (7.5 w) in dry carbon tetrachloride (110 v), the reaction temperature being maintained at 10° to 20°C. The oxime gradually dissolved to give a clear deep blue solution, becoming pale yellow on standing, while hydrogen chloride was evolved. The solvents were stripped off under reduced pressure. The residue (21 w) was treated with about 50 v of hot light petroleum (60°/80°C) and filtered and then had m.p. 95° to 97°C.

Analysis Found Cl 47.0%

$C_7H_4ONCl_3$ requires Cl 47.4%

2-Bromo-α,6-dichlorobenzaldoxime was prepared in a similar way by chlorinating 2-bromo-6-chlorobenzaldoxime. It had a m.p. 110° to 113°C.

Analysis Found: C 31.1, H 1.7, N 5.4, Cl 36.7%

$C_7H_4ONCl_2Br$ requires: C 31.2, H 1.5, N 5.2, Cl 26.4%

α,2-Dichloro-6-fluorobenzaldoxime was prepared in a similar way by chlorinating 6-chloro-2-fluoro benzaldoxime. it had m.p.

EXAMPLE II Preparation of α,2,6-trichlorobenzaldoxime and its O-acetyl derivative [Fig. 4]

Into a suspension of 2,6-dichlorobenzaldoxime (19 w) in carbon tetrachloride (200 v), was passed chlorine until nearly all the

oxime had gone into solution, the temperature of the reaction mixture being kept below 15°C. The green solution obtained was evacuated to remove excess chlorine, the solvent and a volatile substance causing a blue odour, presumably nitrosyl chloride. The residue (21.2 w) partly crystallised on standing. The residue was dissolved in 100 v of hot 60°/80°C. light petroleum. On cooling colorless leaflets (10 w), m. p. 89° to 94°C. were obtained. These were filtered off and recrystallised from 60°/80°C petroleum ether and then had m. p. 93 5° to 94 5°C.

Analysis Found C 37.1, H 1.9%

$C_7H_4ONCl_3$ requires C 37.4, H 1.8%

A yellow oil isolated from the mother liquor has been identified as 2,6-dichlorobenzal dichloride.

The O-acetyl derivative was obtained by heating α,2,6-trichlorobenzaldoxime (10 w and acetic anhydride (10 v) together on a water bath for one hour. The product partly crystallised and the crystals collected by filtration with suction. A second crop was obtained by adding the filtrate to aqueous sodium bicarbonate and filtering. The combined crops were recrystallised from hot glacial acetic acid. The product obtained had m.p. 106°C. Yield 6.5 w.

Analysis Found C 40.2, H 2.3, N 5.4%

$C_9H_6O_2NCl_3$ requires C 40.5, H 2 3, N 5.3%

Example III Preparation of 2,6-dichlorobenzonitrolic acid [Fig. 5]

To a stirred solution of 2,6-dichlorobenzaldoxime (5 w) in glacial acetic acid (50 v), concentrated nitric acid (70% w/w, d 1.42; 2 v) was added dropwise, the temperature of the reaction mixture being kept below 15°C. The mixture was then poured into ice water (300 v) and the aqueous mixture extracted with methylene dichloride. The extract was dried with calcium chloride and the solvent then removed under reduced pressure. The residue was taken up in glacial acetic acid and water then added gradually to the solution. A first precipitate of 2,6-dichlorobenzonitrile N-oxide, m. p. 75° to 77°C., formed by decomposition of some of the nitrolic acid, was separated. Further addition of water precipitated a yellow solid from which the desired nitrolic acid was isolated by extracting the ethereal solution with aqueous ammonia (25% w/v) until the extracts were no longer coloured, and then carefully acidifying the filtered extracts with aqueous sulphuric acid (6N). The resulting precipitate was filtered off with suction, washed with cold water and dried at a low temperature in a vacuum. The temperature throughout the above process was maintained at below 15°C. The product had m.p. 62°C. decomp.

In another preparation, the methylene dichloride extract of the aqueous nitration mixture was extracted 3 times with 30 v portions of 0.5-1.0 N aqueous ammonia until the ammonia extracts were no longer coloured. The combined ammonia extracts, which were deep orange-red in colour, were washed once with 50 v of methylene chloride, filtered and carefully acidified with hydrochloric acid. Aqueous sulphuric or oxalic acid can be used instead of hydrochloric acid. The precipitate which separated was filtered off by suction washed with cold water and dried at a low temperature in a vacuum. The temperature throughout was kept at 10° to 15°C. The product had m. p. 61-2°C. decomp.

Example IV Preparation of α-cyano-2,4-dichlorobenzaldoxime [Fig. 6.].

Sodium (2.3 w) was dissolved in ethanol (80.0 v), the solution cooled to 0°C and amyl nitrite (14.6 v) added. A solution of 2,4 dichlorobenzyl cyanide (19.0 w) in ethanol was then added and the mixture left overnight. The precipitated sodium salt of the α-cyanobenzaldoxime was dissolved in water and treated with dilute acetic acid. The free oxime so obtained was recrystallised from benzene. Yield 13.1 w (55%); m. p. 151°C.

Analysis Found C 44.7, H 2.0, N 13.2%

$C_8H_4ON_2Cl_2$ requires C 44.7, H 1.9, N 13.0%

Example V Preparation of α-cyano-2,6-dichlorobenzaldoxime

To a stirred solution of α,2,6-trichlorobenzaldoxime (6.7 w) in ethanol (50 v) was added gradually a solution of sodium cyanine (2.5 w) in water (10 v) during which the temperature of the mixture rose to about 45°C. The mixture was heated at 50° to 60°C for 30 minutes, then cooled and filtered. The filtrate was evaporated to dryness, the residue dissolved in water, the solution acidified with 3N hydrochloric acid and extracted twice with methyle dichloride (20 v each time). The combined extracts were dried with calcium chloride and evaporated to dryness. The residue was recrystalised from carbon tetrachloride. Yield 3.8 w; m. p. 118° to 120°C.

Analysis Found C 44.6, H 1.8, Cl 33.9%

$C_8H_4ON_2Cl_2$ requires C 43.8, H 1.9, Cl 33.0%

Example VI Preparation of α-thiocyanato-2,6-dichlorobenzal doxime (Fig. 7).

To a solution of α,2,6-trichlorobenzaldoxime (6.7 w) in alcohol (50 v) was added a solution of potassium thiocyanate (5 w) in water (10 v). The temperature of the mixture rose to about 35°C. The mixture was warmed at 50° to 60°C. for 30 minutes, filtered and the filtrate evaporated to dryness. The residue was dissolved in methylene dichloride, the solution washed with water until free from thiocyanate ion, then evaporated to dryness. The residue was recrystallised from carbon tetrachloride. Yield 3.2 w; m. p. 128° to 131°C

Analysis Found: C 37.6, H 2.0, Cl 25.6, S 14.5%

$C_8H_4ON_4Cl_2S$ requires C 38.8, H 1.6, Cl 28.8, S 13.1%

Example VII Preparation of α-phenylsulphonyl-2,6-dichlorobenzaldoxime (Fig. 8)

Solutions of sodium benzenesulphinate dihydrate (10.0 w) in methanol (50 v) and of α,2,6-trichlorobenzaldoxime (10.0 w) in methanol (50 v) were mixed. The precipitate of sodium chloride was filtered off, the filtrate evaporated to dryness and the residue crystallised from benzene. The product obtained (12.8 w) had m.p. 147° to 148°C *decomp.*

Analysis Found: C 47.6, H 2.8, Cl 20.8, S 9.1%

$C_{13}H_9O_3NCl_2S$ requires C 47.2, H 2.7, Cl 21.5, S 9.7%

The product recrystallised from methanol with one molecule of methanol of crystallisation.

Analysis Found: C 46 5, H 3.5, Cl 20.4, S 9.4%

$C_{13}H_9O_3NCl_2S.CH_3OH$ requires C 46.4, H 3.6, Cl 19.6 S 8.9%

Example VIII Preparation of α-(4-methylphenylthio)-2,6-dichlorobenzaldoxime [Fig. 9]

A solution of α,2,6-trichlorobenzaldoxime (6.0 w) in methanol (25 v) was added to a mixture of p-thiocresol (3.2 w) in methanol (10 v) and sodium (0.6 w) dissolved in methanol (10 v). The reaction mixture was kept at 25° to 30°C by external cooling. The colourless precipitate was filtered off and washed with water.

Yield 7.3 w; m. p. 211°C.

Analysis: Found C 53.2, H 4.3, S 10.3%

$C_{14}H_{11}ONSCl_2$ requires C 53.8, H 3.5, S 10.3%

Example IX Preparation of α-amino-2,6-dichlorobenzaldoxime [Fig 10]

To a solution of α,2,6-trichlorobenzaldoxime (1 mol.) in absolute alcohol was added dry ammonia (2 mol.) in absolute alcohol. Ammonium chloride separated and was filtered off. More ammonium chloride separated on adding ether to the filtrate and was also removed. Dry hydrogen chloride (0.1 mol) in ether was added to the filtrate. Colourless crystals, m. p. 220°C of the desired hydrochloride separated on standing. Yield 75% theory.

Analysis Found Cl 44.0%

$C_7H_7ON_2Cl_3$ requires Cl 44.1%

The hydrochloride was dissolved in a little distilled water and the theoretical quantity of sodium hydroxide dissolved in a little water added with stirring. The free amine precipitated immediately as a colourless solid. This was filtered off, washed free from salt with cold water and product dried and recrystallised from methanol. It had m.p. 167°C. Quantitative yield.

Analysis Found : C 41.2, H 3.0%

$C_7H_6ON_2Cl_3$ requires C 41.0, H 2.9%

The following salts were prepared in 5% aqueous solution by reacting α-amino-2,6-dichlorobenzaldoxime (B) with the equivalent amount of acid in water :—$B.\frac{1}{2}H_2SO_4$, $B.H_3PO_4$, $B.HNO_3$, $B_2.(COOH)_2$, $B.HClO_4$.

Example X α-Amino-2,4-dichlorobenzaldoxime hydrochloride (m.p. 190°C. *decomp.*) was prepared from α,2,4-trichlorobenzaldoxime by a process analogous to that described in Example IX.

Example XI α-Amino-2-chloro-6-fluorobenzaldoxime (m.p. 131° to 134°C.) and its hydrochloride (m.p. 195° to 127°C. *decomp.*) were prepared from α,2-dichloro-6-fluorobenzaldoxime by a process analogous to that described in Example IX.

Analysis Base Found : Cl 18.8%

$C_7H_6ON_2ClF$ requires Cl 18·8%

Hydrochloride Found :Cl 31.8%

$C_7H_5ON_2Cl_2F$ requires Cl 31.6%

Example XII α-Amino-2-bromo-6-chlorobenzaldoxime (m. p. 175° to 178°C.) was prepared from 2-bromo-α,6-dichlorobenzaldoxime by a process analogous to that described in Example IX.

Analysis Found C 33.1, H 2.6, N 11.3%

$C_7H_6ON_2Cl_2Br$ requires C 33.7, H 2.4, N 11.2%

Example XIII Preparation of α-piperidyl-2,6-dichlorobenzaldoxime [Fig. 11].

Piperidine (2 mol.) was added gradually to a solution of α,2,6-trichlorobenzaldoxime (1 mol.) in dry ether at room temperature. Piperidine hydrochloride separated and was filtered off and the ether removed from the filtrate. The residue was recrystallised from methanol and the product then obtained as colourless crystals m. p. 172°C in quantitative yield.

Analysis Found Cl 25.9%

$C_{12}H_{14}ON_2Cl_2$ requires Cl 26.0%

By replacing piperidine in the above process by the bases stated below, the following α-substituted-2,6-dichlorobenzaldoximes were prepared. The hydrochlorides were prepared by the method of Example IX.

Base	α-substituent	m.p. °C	Analysis Found C	H	Cl	Theory C	H	Cl
diethanolamine	$-N_2(CH_2.CH_2.OH)_2$	135	45.0	4.8		45.0	4.8	
ethanolamine	$-NHCH_2.CH_2OH$	175	43.2	4.2	29.2	43.4	4.0	28.6
allylamine	$-NHCH_2CH-CH_3$	125	49.7	4.2	29.9	49.0	4.1	29.0
	$-NH.CH_2.CH-CH_2.HCl$.	207 decomp.		38.2			37.9	
methylamine	$-NHCH_3$	162	43.1	3.7		43.8	3.7	
	$-NHCH_3.HCl$	207 decomp.		42.2			41.7	
dimethylamine	$-N(CH_3)_2$	122	46.2	4.4		46.4	4 3	
isobutylamine	$-NH.CH_2.CH(CH_3)_2$	143	50.2	5.5		50.6	5.4	
morpholine	$-N<\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}>O$	160		26.2			25.8	

Example XIV Preparation of α-hydroxylamine-2,6-dichlorobenzaldoxime hydrochloride [Fig. 12].

A solution of α,2,6-trichlorobenzaldoxime (5 w ; 1 mol.) in ethanol (50 v) was added to a solution of hydroxylamine (2.1w; 2 mol.) in ethanol (50 v) at room temperature. The reaction mixture was concentrated to low volume at room temperature under reduced pressure. Dry ether was then added and the precipitated hydroxylamine hydrochloride was filtered off. A solution of excess hydrogen chloride in dry ether was added to the filtrate and the precipitated α-hydroxilamino-2,6-dichlorobenzaldoxime hydrochloride was separated and recrystallised from a mixture of ethanol and benzene, the purified product being obtained in 50% yield. It had m. p. 170°C. decomp.

Analysis Found Cl 41.5%

$C_7H_7O_2N_2Cl_3$ requires Cl 41.4%

Example XV Preparation of α-hydrazino-2,6-dichlorobenzaldoxime [Fig. 13]

Hydrazine hydrate (11 w of 18% w/w) in ethanol (10 v) was added to α,2,6-trichlorobenzaldoxime (12.5 w) in ethanol (100 v). Hydrazine hydrochloride (2.5 w) separated after some time and was filtered off. The filtrate was evaporated to dryness and the oily residue shaken with water for 3 hours. A pink solid formed and was filtered off (4.7 w). It was recrystallised from a mixture of ether and methanol. The product obtained decomposed at 108° to 109°C.

Analysis Found C 38.3, H 3.4, Cl 31.8%

$C_7H_7ON_3Cl_2$ requires C 38.2, H 3.2, Cl 32.3%

From the ether-methanol mother liquor, an unidentified crystalline material m.p. 144° to 145°C was recovered.

Example XVI Preparation of α-phenylhydrazino-2,6-dichlorobenzaldoxime [Fig. 14].

Phenylhydrazine (2 mol.) was added to a solution of α,2,6-trichlorobenzaldoxime (1 mol.) in dry ether. Phenylhydrazine hydrochloride separated immediately. It was filtered off and the ethereal filtrate evaporated. The residue was recrystallised from methanol and then had m.p. 147°C. Yield 80% theory.

Analysis Found Cl 24.2%

$C_{13}H_{11}ON_3Cl_2$ requires Cl 24.0%

Example XVII Preparation of α-amino-2-chloro-6-methylbenzaldoxime and its hydrochloride [Fig. 15].

A mixture of 2-chloro-6-methylbenzonoitrile (11.5 w), hydroxylamine hydrochloride (10.4 w), potassium carbonate (anhy-

drous 10.4 w), isopropanol (100 v) and water (50 v) was refluxed for 53 hours. The reaction mixture was then steam distilled to remove isopropanol and unchanged nitrile (1 w) and then cooled, whereupon 2-chloro-6-methylbenzamide (6.2 w ; m. p. 167° to 172°C) separated.

The mother liquor was concentrated under reduced pressure, then made alkaline with concentrated aqueous sodium hydroxide solution and the mixture extracted with ether. The ethereal extract was dried with calcium chloride and a dry solution of hydrogen chloride in ether was added. The resulting precipitate was filtered off, washed with ether and dried. Yield 3.5w, ; decomposes at 193°C.

Analysis C Found 43.8, H 4.8, N 12.8, Cl 31.5%

$C_8H_{10}ON_2Cl_2$ requires C 43.4, H 4.5, N 12.7, Cl 32.1%

Example XVIII Preparation of α-ureido-2,6-dichlorobenzaldoxime [Fig. 16].

An aqueous solution of 2,6-dichloro-α-aminobenzaldoxime hydrochloride was treated with an aqueous solution of potassium cyanate. The ureido compound precipitated immediately. It was filtered off and recrystallized from ethanol. The product had m.p. 190°C. Yield 97.5% theory.

Analysis Found Cl 28.4%

$C_8H_7O_4N_3Cl_2$ requires Cl 28.6%

α-Ureido-2,4-dichlorobenzaldoxime was prepared in a similar way from 2,4-dichloro-α-aminobenzaldoxime. After recrystallisation from aqueous alcohol, the product had m. p. 165°C. Yield practically quantitative.

Analysis Found C 38,7. H 3.2%

$C_8H_7O_3Cl_2$ requires C 30.7, H 2.7%

Example XIX Preparation of α-[2-trichloro-1-hydroxyethylamino]-2,6-dichlorobenzaldoxime [Fig. 17].

α-Amino 2,6-dichlorobenzaldoxime (10.3 w) was dissolved in hot benzene and treated with anhydrous chloral (5 v). On cooling, the desired product precipitated and was filtered off and recrystallised once from benzene. It then had m.p. 162°C. Yield practically quantitative.

Analysis Found C 30.9, H 2.1, N 7.6, Cl 49.8%

$C_9H_7O_2N_2Cl_5$ requires C 30.6, H 2.0, N 7.9, Cl 50.3%

Example XX Preparation of O-trichloroacetyl-α-amino-2,6-dichlorobenzaldoxime [Fig. 18].

Trichloroacetyl chloride (9.1 w) in dry ether (30 v) was added gradually to a stirred solution of α-amino-2,6-dichlorobenzaldoxime (10.3 w) and triethylamine (5.1) in dry ether (70 v). Triethylamine hydrochloride was precipitated and was filtered from the mixture. The filtrate was concentrated and the desired product crystallised from the concentrate as colourless crystals, m.p. 163°C.

Analysis Found C 43.0, H 3.6%

$C_{10}H_{10}O_3N_2Cl_2$ requires C 43.3, H 3.6%

Example XXI Preparation of O-ethoxycarbonyl-α-amino-2,6-dichlorobenzaldoxime [Fig. 19].

Ethyl chloroformate (5.5 w) in dry ether (30 v) was added gradually to a stirred solution of α-amino-2,6-dichlorobenzaldoxime (10.3 w) and triethylamine (5.1 w) in dry ether (70 v). The precipitate of triethylamine hydrochloride formed was filtered off and the filtrate concentrated. The desired product separated from the concentrate in colourless crystals, m. p. 163°C.

Analysis Found C 43.0, H 3.6%

$C_{10}H_{10}O_3N_2Cl_2$ requires C 43.3, H 3.6%

Compounds of the general formula shown in Fig. 1 in which Y represents a cyano group have negligible herbicidal activity but very high fungicidal activity. They are particularly toxic to bunt (Tilletia caries), a seed-borne fungus infection, and in this compare very favourably with the organo mercurial standard fungicides used in seed-dressings for combatting this fungus. Thus, compared with the standard fungicide comprising 7:1 to 15:1 parts by weight mixtures of phenylmercury acetate and ethylmercury chloride, 2,6-dichloro-α-cyanobenzaldoxime is equally effective in controlling bunt while 2,4-dichloro-α-cyanobenzaldoxime is more effective. 2,4-Dichloro-α-cyanobenzaldoxime is not only effective as a seed disinfectant but is also effective as a seed protectant. Pea and bean seeds treated with a dust containing 50% by weight of this compound and an inert filler at the rate of 2 grams per kilgoram of seed and then planted in Pythium infested soil receive the same degree of protection against this damping-off organism as is given by TMTD (tetramethylthiuram disulphide) dust. The α-cyanobenzaldoximes have the great advantage over the organo mercurial fungicides in possessing relatively low mammalian toxicity. Thus, 2,6-dichloro-α-cyanobenzaldoxime is non-toxic to rats at a dosage of 64 milligrams per kilogram of body weight. These α cyanobenzaldoximes are therefore preferred compounds of the invention. Seed dressing compositions containing said α-cyanobenzaldoximes as a fungicidal ingredient are a further feature of the invention. These compositions may contain one or more other pesticides, particularly fungicides or insecticides. Advantageously, dimethylformamide is a component of these compositions. The use of these α-cyanobenzaldoximes and of compositions containing them, as fungicides particularly for the dressing of seed for the control of bunt, is included in the scope of the invention.

High herbicidal activity is exhibited by compounds of the general formula shown in Fig. 1 which are substituted in the α-position by halogen, preferably chlorine or bromine, or by thiocyano or nitro groups. Other highly active herbicidal compounds are those substituted in the α-position by hydroxylamino, amino, substituted amino, hydrazino or ureido groups, the salts of these compounds, for example, the hydrochlorides, sulphates, nitrates etc. being comparable with the bases in activity. The results of herbicidal tests carried out with some of the more active compounds of the invention are summarised in the following Table. These tests were carried out as follows :—

Aqueous compositions containing acetone (40 v), water (60 v), Triton X 155 (0.5% w/v) and the benzaldoxime derivative in logarithmically varying concentrations were used. In the soil spray and soil drench tests, imbibed seeds of oats (O) and mustard (M). and seedling plants of oats, mustard and linseed (O, M, L) respectively, in sterile No. 1 John Innes compost, were sprayed at 50 gallons per acre or drenched at 1000 gallons per acre. In the foliage test, similar plants of oats, mustard and linseed were sprayed with a volume equivalent to 50 gallons per acre. Control tests in which seeds or plants were sprayed and/or drenched with the aqueous acetone — Triton X 155 solution only were also carried out. The phytotoxic effect of the benzaldoxime applied was assessed by determining the reduction from the control in fresh weight of stem and leaf of test plants and a regression curve relating growth inhibition and dosage plotted. The dosage of the benzaldoxime derivative required for 50% (G. I. D. 50) and 90% (G. I. D. 90) inhibition of foliage growth is given in the Table. Dosages greater than 10 pounds per acre are indicated by X. It can be seen from the Table that most of the benzaldoxime derivatives cause 90% growth inhibition of the soil spray test at dosages of 2 pounds per acre or less. 2,6-dichloro-α-aminobenzaldoxime hydrochloride being outstanding.

It can be seen further that most of the compounds have similar degrees of activity to both monocotyledons and dicotyledons so that these compounds are effective total pre-emergence herbicides. The Table also shows the very low herbicidal activity of 2,6-dichloro-α-cyanobenzaldoxime referred to previously as a fungicide.

The invention also relates to a method of protecting crop plants from undesirable competition with weeds or from attack by seed- or soil-borne fungus diseases which comprises pretreating the soil in which the crop is to be grown with an α-substituted benzaldoxime of the invention having as the α substituent a halogen, preferably chlorine or bromine atom, a thiocyano or nitro group, or a hydroxylamino, amino, substituted amino, hydrazino or ureido group, as the free base or in salt form, or with an α-cyanobenzaldoxime respectively.

TABLE

HERBICIDAL ACTIVITY OF SOME α-SUBSTITUTED BENZALDOXIMES.

NAME	50% GROWTH INHIBITION DOSE LB/ACRE								90% GROWTH INHIBITION DOSE LB/ACRE.							
	SEEDS		PLANTS						SEEDS		PLANTS					
	SOIL SPRAY		FOLIAR SPRAY			SOIL DRENCH			SOIL SPRAY		FOLIAR SPRAY			SOIL DRENCH		
	O	M	O	M	L	O	M	L	O	M	O	M	L	O	M	L
α-Hydrazino-2, 6-dichlorobenzaldoxime	<2.9	<2.9	<2.4	X	X	<2.4	X	X	<2.9	<2.9	X	X	X	X	X	X
α-Phenylhydrazino-2,6, dichlorobenzaldoxime	2.2	8.4	X	X	X	X	X	X	4.8	X	X	X	X	X	X	X
α-Ureido-2,6-dichlorobenzaldoxime	1.1	2.8	X	X	X	2.0	X	X	1.7	7.0	X	X	X	X	X	X
α-4-Methylphenylthio-2,6-dichlorobenzaldoxime	9.8	9.1	X	X	X	X	X	X	X	X	X	X	X	X	X	X
α-Benzenesulphonyl-2,6-dichlorobenzaldoxime	8.3	X	X	X	X	3.9	X	7.4	5.3	X	X	X	X	8.5	X	X
O-Acetyl-α-2,6-dichlorobenzaldoxime	<0.9	<0.9	X	X	X	3.6	X	X	<0.9	<0.9	X	X	X	X	X	X
α-Methylamino-2,6-dichloro-benzaldoxime	2.3	4.1	X	X	X	6.2	X	5.8	3.4	6.3	X	X	X	X	X	X
α-Methylamino-2,6-dichlorobenzaldoxime HCl	1.1	4.4	X	X	X	6.6	X	X	2.1	X	X	X	X	X	X	X
α-Dimethylamino-2,6-dichlorobenzaldoxime	1.8	2.7	X	X	X	5.7	X	6.2	3.2	3.9	X	X	X	X	X	X
α Allylamino-2,6-dichloro benzaldoxime	2.4	4.7	X	X	X	4.2	7.0	2.1	3.3	7.1	X	X	X	X	X	X
α-Allylamino-2,6-dichloro benzaldoxime hydrochloride	0.9	1.9	X	X	5.5	1.4	6.6	2.9	1.7	3.3	X	X	X	X	X	X
α-Iso-butylamino 2,6-dichloro benzaldoxime	1.8	3.8	X	X	X	5.0	X	X	3.3	6.3	X	X	X	X	X	X
α-Ethanolamino-2,6-dichloro-benzaldoxime	2.0	2.6	X	X	X	5.0	8.0	6.7	3.5	3.7	X	X	X	X	X	X
α-Diethanolamine-2,6-dichloro benzaldoxime	.1	6.5	X	X	X	6.6	X	X	1.0	9.8	X	X	X	X	X	X
α- hloro-2,6-dichloro-benzaldoxime	<2	2.4	X	<1	3.9	5.0	X	X	<2	6.9	X	3.6	6.2	10.0	X	X
α-Cyano-2,6-dicholoro-benzaldoxime	7.9	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
α-Thiocyanato-2,6-dichloro-benzaldoxime	<2.9	<2.9	4.5	X	X	2.8	6.5	X	<2.9	<2.9	8.6	X	X	X	X	X
α-Nitro-2,6-dichloro benzaldoxime	<2	<2	<1	<1	X	<1	<1	2.0	<2	<2	9.0	9.2	X	7.4	7.2	8.5
2,6-Dichloro-α-hydroxylamino-benzaldoxime hydrochloride	0.6	<0.9	X	4.4	X	1.2	5.4	3.0	1.1	1.8	X	8.8	X	X	X	X
α-Amino-2,6-dichloro-benzaldoxime	<0.6	1.4	5.4	6.7	X	6.8	X	X	2.0	2.8	X	X	X	X	X	X
α Amino-2,6-dichloro-benzaldoxime hydrochloride	<0.6	<0.6	2.1	7.2	X	<1	2.8	4.0	<0.62	1.2	X	X	X	X	X	X

α,2,6-Trichlorobenzaldoxime, in addition to its high fungicidal activity is also very toxic to aquatic snails, particularly to Australorbis glabratus, Planorbis corneus and Bulinus truncatus, which are known carriers of the parasite carrying bilharziasis in man. α,2,4,6-Tetrachlorobenzaldoxime and its O-acetyl derivative, α-benzene-sulphonyl-2,6-dichlorobenzaldoxime and O-acetyl-α,2,6-trichlorobenzaldoxime are also effective molluscicides. These compounds cause the death of snails in 24 hours at dosages of as little as one part per million.

This invention relates further to compositions comprising an α-substituted benzaldoxime as hereinbefore specified and a carrier or a surface active agent or a carrier and a surface active agent.

The term "carrier" as used herein means a material, which may be inorganic or organic and synthetic or of natural origin, with which the active substance is mixed or formulated to facilitate its storage, transport and handling and its application to the plant, seed, soil or other object to be treated. The carrier is preferably biologically and chemically inert. It may be a solid or fluid. Solid carriers are preferably particulate, granular or pelleted though other shapes and sizes are not thereby excluded. Solid carriers, generally obtainable in particulate, granular or pelleted form, may be naturally occurring minerals, though they may have been subjected to grinding, sieving, purification and other treatments, for example, gypsum, tripolite, diatomite, mineral silicates such as mica, vermiculite, talc and pyrophylite and clays of the montmorillonite, kaolinite or attapulgite groups, calcium or magnesium limes or calcite and dolomite. Carriers produced sythetically, for example, synthetic hydrated silicon oxides and synthetic calcium silicates may also be used and many proprietary products of this type are available commercially. The carrier may also be an elemental substance such as sulphur or carbon, preferably an activated carbon. If the carrier possesses intrinsic catalytic acidity such that it would decompose the toxicant it is advantageous to incorporate a stabilizing agent, for example, urea or hexamethylene tetramine, to neutralise this acidity and so prevent possible decomposition of the benzaldoxime.

For some purposes, a resinous or waxy carrier may be used, preferably one which is solvent soluble or thermoplastic, including fusible. Examples of such carriers are natural or synthetic resins such as a coumarone resin, rosin, copal, shellac, dammar, polyvinyl chloride, styrene, polymers and copolymers, a solid grade of polychlorophenol such as is available under the Registered Trade Mark "Aroclor", a bitumen, an asphaltite, a wax, for example, beeswax or a mineral wax such as paraffin wax or Montan wax, or a chlorinated mineral wax. Compositions comprising such resinous or waxy carriers are preferably in granular or pelleted form.

Fluid carriers may be liquids, for example water, or an organic fluid including a liquefied normally vaporous or gaseous material, or a vaporous or gaseous material, and may be solvents or non-solvents for the active material. Horticultural petroleum spray oils boiling in the range 275° to 575°F or boiling in the range 575° to 1000°F and having an unsulphonatable residue of at least 75% and preferably of at least 90%, or a mixture of these two types of oil are particularly suitable liquid carriers.

The carrier may also be a simple or compound fertilizer which may be a solid, preferably granular or pelleted, or a liquid, for example an aqueous solution.

The carrier may be mixed or formulated with the active material during its manufacture or at any stage subsequently. The carrier may be mixed or formulated with the active material in any proportion. One or more carriers may be used.

The compositions of the invention may be concentrates, suitable for storage or transport and containing, for example, from 10 to 95% by weight of the substituted benzaldoxime. These can be diluted with the same or a different carrier to a concentration suitable for application. The compositions of the invention may also be dilute compositions suitable for application. In general, concentrations of 0.01 to 05% by weight, of active material based on the total weight of the composition are satisfactory, though lower and higher concentrations can be applied if necessary. Effective weed control is obtainable by applying the compositions at the rate of 1 to 20 pounds per acre of a herbicidally active benzaldoxime.

The compositions of the invention may be formulated as dusts. These comprise an intimate mixture of the benzaldoxime and a finely powdered solid carrier such as is indicated above. These powder carriers may be oil-treated to improve adhesion to the surface to which they are applied. These dusts may be concentrates, in which case a highly sorptive carrier is preferably used. These require to be diluted with the same or a different finely powdered carrier, which may be of lower sorptive capacity, to a concentration suitable for application.

The compositions of the invention may be formulated as wettable powders comprising a major proportion of the benzaldoxime mixed with a dispersing, i.e. deflocculating or suspending, agent and, if desired, a finely divided solid carrier. The benzaldoxime may be in particulate form or adsorbed on the carrier and preferably constitutes at least 10% more preferably at least 50% by weight of the composition. The concentration of the dispersing agent should in general be between 0.1 and 10% by weight of the total composition though larger or smaller amounts may be used if desired.

The dispersing agent used in the composition of the invention may be any substance having definite dispersing, i.e. deflocculating or suspending, properties as distinct from wetting properties, although these substances may also possess wetting properties.

The dispersing agent used may be protective colloid such as gelatin, glue, casein, gums or a synthetic polymeric material such as polyvinyl alcohol. Preferably, however, the dispersing agents used are sodium or calcium salts of high molecular weight sulphonic acids, e.g. the sodium or calcium salts of lignin sulphonic acids derived from sulphite cellulose waste liquors. The calcium or sodium salts of condensed aryl sulphonic acids, for example the product known as "Tamol 731", are also suitable.

The dispersing agents used may be non-ionic emulsifiers, for example the condensation products of fatty acids containing at least 12, preferably 16 to 20, carbon atoms in the molecule, or of abietic acid or naphthenic acids obtained in the refining of petroleum lubricating oil fractions, with alkylene oxides such as ethylene oxide or propylene oxide or with both ethylene oxide and propylene oxide as, for example, the condensation product of oleic acid and ethylene oxide containing 6 ethylene oxide units in the molecule. Partial esters of the above acids with polyhydric alcohols such as glycerol, polyglycerol, sorbitol or mannitol may also be used.

The dispersing agents referred to above may also possess wetting properties but in general it is preferable to incorporate two separate surface active agents, one having particularly good dispersing properties and the other having particularly good wetting properties. The actual amount of wetting agent incorporated can be varied considerably and in general is from 0 to 10% by weight based on the total composition.

Suitable wetting agents include the alkali metal salts, preferably sodium salts, of sulphuric acid esters or sulphonic acids containing at least 10 carbon atoms in the molecule, for

example, the sodium secondary alkyl sulphates available under the Registered Trade Mark 'Teepol", sodium salts of sulphonated castor oil, sodium dodecyl benzene sulphonate. Non-ionic wetting agents may also be employed for example, polyalkylene oxide polymers, e.g. the "Pluronics", and condensation products of polyalkylene oxides with aromatic nuclei (e.g. octyl cresol).

Granulated or pelleted compositions comprising a suitable carrier having a benzaldoxime incorporated therewith are also included in the invention. These may be prepared by impregnating a granular carrier with a solution of the benzaldoxime or by granulating a mixture of a finely divided solid carrier and the benzaldoxime. The carrier used may consist of or contain a fertiliser or fertiliser mixture, for example superphosphate.

The compositions of the invention may also be formulated as solutions of benzaldoxime in an organic solvent or mixture of solvents, for example of alcohols, ketones especially acetone, ethers, hydrocarbons. Fungicidal compounds of the invention to be used as seed dressings are preferably dissolved in dimethylformamide (DMF) or in a mixture of dimethylformamide and methanol. A suitable seed dressing formulation comprises for example, 1 to 10% w/v of α-cyano-2,6-dichlorobenzaldoxime and 99 to 90% of DMF or 1:1 mixture of DMF and methanol. Petroleum hydrocarbon fractions used as solvents should preferably have a flash point above 73°F, for example, a refined aromatic extract of kerosine. For use in application of fungicidal compounds to foliage the solvent used should not be phytotoxic and for this purpose a petroleum spray oil boiling in the range 275° to 575°F or boiling in the range 575° to 1000°F and having an unsulphonatable residue of at least 75% and preferably of at least 90%, or a mixture of these types of oil, is preferably used. Auxiliary solvents such as alcohols, ketones and polyalkylene glycol ethers and esters may be used in conjuction with these petroleum solvents. Such oil solutions are particularly suitable for application by low volume spraying for example at the rate of 5 to 10 gallons per acre. They may also be diluted with a cheap solvent for high volume spraying.

Compositions of the present invention may also be formulated as emulsifiable concentrates which are concentrated solutions or dispersions of the benzaldoxime in an organic liquid, preferably a water-insoluble organic liquid, containing an added emulsifying agent. These concentrates may also contain a proportion of water for example up to 50% by volume, based on the total composition (i.e. a "mayonnaise" composition) to facilitate subsequent dilution with water. Suitable organic liquids are for example the above petroleum hydrocarbon fractions as described above.

The emulsifying agent may be of the type producing water-in-oil type emulsions which are suitable for application by low volume spraying, or an emulsifier of the type producing oil-in-water emulsions may be used, producing concentrates which can be diluted with relatively large volumes of water for application by high volume spraying. In such emulsions, the benzaldoxime is preferably in the non-aqueous phase.

Suitable types of emulsifier for use in these emulsions or emulsifiable concentrates are the non-ionic and anionic dispersing and wetting agents described above, also suitable are long chain alkyl ammonium salts and alkyl sulpho-succinates.

The concentration of emulsifier used will in general be within the limits 0.5% and 25.0% based on the final composition.

The compositions of the invention may contain other ingredients, for example, water conditioning agents for example sodium polyphosphates or cellulose ethers, other herbicides, pesticides or stickers, for example a non-volatile oil.

Aqueous dispersions and emulsions, for example, compositions obtained by diluting the wettable powders or emulsifiable concentrates of the present invention with water also lie within the scope of the present invention.

WE CLAIM :—

1. A pesticidal composition comprising as active ingredient one or more alpha-substituted benzaldoximes of the general formula shown in Fig. 1 of the accompanying drawings and salts thereof, wherein X represents a halogen atom ;

W represents a halogen atom or an alkyl group ;

n is 1, 2, 3 or 4 ;

Y represents a halogen atom or a hydroxy, hydrocarbyloxy, cyano thiocyano, or nitro group or a group of formula -COOR' or $-SO_2R'$ wherein R' represents a hydrogen atom or a hydrocarbyl group ; or Y represents a group of formula $-NR^1R^2$ wherein R^1 and R^2 may be the same or different, each representing a hydrogen atom, a hydrocarbyl group, a hydrocarbyl group substituted by halogen or hydroxyl or a hydrocarbyl group substituted by halogen and hydroxyl, or R^2 represents a hydrogen atom or a hydrocarbyl group and R^3 represents a hydroxyl group or the group $-NR^3R^4$ wherein R^3 and R^4 may be the same or different, each representing a hydrogen atom or a hydrocarbyl group ; or Y represents a group of formula $-NR^4.CO.NR^5R^7$ or $-NR^4.CS.NR^6.R^7$, or a tautomeric form thereof, wherein R^4, R^6 and R^7 may be the same or different, each representing a hydrogen atom or a hydrocarbyl group ; or Y represents a group of formula $-SR^8$ or $-SO_xR^9$ wherein *x* is 1 or 2 and R^8 represents a hydrogen atom or R^8 and R^9 each represent a hydrocarbyl group, or a hydrocarbyl group substituted by halogen, Z represents a hydrogen atom, and acyl group or an alkoxylcarbonyl group, in admixture with a solid carrier as hereinbefore defined and/or a surface active agent, or in admixture with a liquid carrier and a surface active agent.

2. A composition as claimed in claim 1 containing a benzaldoxime of the said formula wherein X represents a chlorine atom.

3. A composition as claimed in claim 1 or 2 containing a benzaldoxime of the said general formula wherein W represents a substituent in at least one of positions 4 or 6 of the benzene nucleus.

4. A composition as claimed in claim 1, 2 or 3 containing a benzaldoxime of the said general formula wherein W represents a chlorine or bromine atom.

5. A composition as claimed in claim 1, 2 or 3 containing a benzaldoxime of the said general formula wherein W represents a methyl group.

6. A composition as claimed in any one of the preceding claims containing a benzaldoxime of the said general formula wherein the hydrocarbyl group which R^1 or R^2 may represent is an alkyl group of 1 to 4 carbon atoms, or a hydroxy or halogen substituted or hydroxy and halogen substituted alkyl group of 1 to 4 carbon atoms.

7. A composition as claimed in claim 6 containing a benzaldoxime of the said general formula wherein R^1 represents the group $-CHOH.CCl_3$ or $-CHOH.CBr_3$.

8. A composition as claimed in claim 6 containing a benzaldoxime of the said general formula wherein R^1 or R^2 or R^1 and R^2 each represent the group $—CH_2.CH_2CH$.

9. A composition as claimed in any one of claims 1 to 5 containing a benzaldoxime of the said general formula wherein R^3 or R^4 represents a phenyl or alkyl phenyl group.

10. A composition as claimed in any one of claims 1 to 5 containing a benzaldoxime of the said general formula wherein R_5 R^6 and R^7 each represent a hydrogen atom.

11. A composition containing one or more salts of basic benzaldoximes as claimed in any one of claims 1 to 10 and an acid.

12. A composition as claimed in any one of claims 1 to 5 containing a benzaldoxime of the said general formula wherein R^8 and R^9 each represent a phenyl or alkylphenyl group.

13. A composition as claimed in any one of the preceding claims containing a benzaldoxime of the said general formula wherein Z represents an acetyl group or a mono-, di- or trichloroacetyl group, or an alkoxycarbonyl group of 2 to 4 carbon atoms.

14. A composition as claimed in any one of claims 1 to 10 and 11 containing one or more alkali or alkaline earth metal, ammonium or substituted ammonium salts of acidic benzaldoximes.

15. A composition as claimed in claim 1 containing alpha, 2,4, trichlorobenzaldoxime as active ingredient.

16. A composition as claimed in claim 1 containing alpha, 2,6-trichlorobenzaldoxime and/or its 0-acetyl derivative as active ingredient.

17. A composition as claimed in claim 1 containing alpha, 2,4,6-tetrachlorobenzaldoxime and/or its 0-acetyl derivative as active ingredient.

18. A composition as claimed in claim 1 containing alpha, 2-dichloro-6-bromobenzaldoxime as active ingredient.

19. A composition as claimed in claim 1 containing 2,6-dichlorobenzonitrolic acid as active ingredient.

20. A composition as claimed in claim 1 containingalpha-cyano-2,6-dichlorobenzaldoxime as active ingredient.

21. A composition as claimed in claim 1 containing alpha-thiocyanato-2,6-dichlorobenzaldoxime as active ingredient.

22. A composition as claimed in claim 1 containing alpha-phenylsulphonyl-2,6-dichlorobenzaldoxime as active ingredient.

23. A composition as claimed in claim 1 containing alpha-(4-methylphenylthio)-2,6-dichlorobenzaldoxime as activc ingredient.

24. A composition as claimed in claim 1 containing alpha-amino-2,6-dichlorobenzaldoxime as active ingredient.

25. A composition as claimed in claim 1 containing alpha-amino-2,6-dichlorobenzaldoxime hydrochloride as active ingredient.

26. A composition as claimed in claim 1 containing alpha-amino-2,6-dichlorobenzaldoxime sulphuric acid salt as active ingredient.

27. A composition as claimed in claim 1 containing alpha-amino-2,6-dichlorobenzaldoxime phosphoric acid salt as active ingredient.

28. A composition as claimed in claim 1 containing alpha-amino-2,6-dichlorobenzaldoxime nitric acid talt as active ingredient.

29. A composition as claimed in claim 1 containing alpha-amino-2,6-dichlorobenzaldoxime perchloric acid salt as active ingredient.

30. A composition as claimed in claim 1 containing alpha-amino-2,6-dichlorobenzaldoxime oxalic acid salt as active ingredient.

31. A composition as claimed in claim 1 containing alpha-piperidyl-2,6-dichlorobenzaldoxime as active ingredient.

32. A composition as claimed in claim 1 containing alpha-bis-(2'-hydroxyethyl) amino-2,6-dichlorobenzaldoxime as active ingredient.

33. A composition as claimed in claim 1 containing alpha-2'-hydroxyethylamino-2,6-dichlorobenzaldoxime as active ingredient

34. A composition as claimed in claim 1 containing 2-allylamino-2,6-dichlorobenzaldoxime as active ingredient.

35. A composition as claimed in claim 1 containing alpha-methylamino-2,6-dichlorobenzaldoxime as active ingredient.

36. A composition as claimed in claim 1 containing alpha-dimethylamino-2,6-dichlorobenzaldoxime as active ingredient.

37. A composition as claimed in claim 1 containing alpha-isobutylamino-2,6-dichlorobenzaldoxime as active ingredient.

38. A composition as claimed in claim 1 containing alpha-morpholino-2,6-dichloro bezaldoxime as active ingredient.

39. A composition as claimed in claim 1 containing alpha-hydroxylamino-2,6-dichlorobenzaldoxime as active ingredient.

40. A composition as claimed in claim 1 containing alpha-hydrazino-2,6-dichlorobenzaldoxime as active ingredient.

41. A composition as claimed in claim 1 containing alpha-phenylhydrazino-2,6-dichlorobenzaldoxime as active ingredient.

42. A composition as claimed in claim 1 containing alpha-amino-2-fluoro-6-chlorobenzaldoxime as active ingredient.

43. A composition as claimed in claim 1 containing alpha-amino-2-chloro-6-bromobenzaldoxime as active ingredient.

44. A composition as claimed in claim 1 containing alpha-amino-2-methyl-6-chlorobenzaldoxime as active ingredient.

45. A composition as claimed in claim 1 containing alpha-(2-trichloro-1-hydroxyethylamino)-2,6-dichlorobenzaldoxime as active ingredient.

46. A composition as claimed in claim 1 containing alpha-amino-0-acetyl-2,6-dichlorobenzaldoxime as active ingredient.

47. A composition as claimed in claim 1 containing alpha-amino-0-trichloroacetyl-2,6-dichlorobenzaldoxime as active ingredient.

48. A composition as claimed in claim 1 containing alpha-amino-0-ethoxycarbonyl-2,6-dichlorobenzaldoxime as active ingredient.

49. A composition as claimed in claim 1 containing alpha-ureido-2,6-dichlorobenzaldoxime as active ingredient.

50. A composition as claimed in claim 1 containing the hydrochloride of the compound claimed in any one of claims 41 to 49 as active ingredient.

51. A composition as claimed in claim 1 containing the alkali metal salt of the oxime claimed in any one of claims 15 to 24 and 31 to 49 as active ingredient.

52. A composition as claimed in any one of claims 1 to 51 formulated as a dust and comprising an intimate mixture of said benzaldoxime and a finely powdered solid carrier.

53. A composition as claimed in any one of claims 1 to 51 formulated as a wettable powder comprising said benzaldoxime, a dispersing agent and if desired a finely divided solid carrier.

54. A composition as claimed in claim 53 containing also a wetting agent.

55. A composition as claimed in any one of claims 1 to 51 comprising said benzaldoxime and an inorganic, resinous or waxy carrier in the form of granules or pellets.

56. A composition as claimed in any one of claims 1 to 51 which is a solution of said benzaldoxime in a solvent or solvent mixture.

57. A composition as claimed in any one of claims 1 to 51 which is an emulsifiable concentrate comprising said benzaldoxime, a solvent therefor and an emulsifying agent.

58 A composition as claimed in any one of claims 1 to 51, which is an aqueous dispersion or emulsion of said benzaldoxime.

59. Aqueous compositions obtained by diluting the wettable powders or emulsifiable concentrates claimed in claims 53, 54, 57 or 58 with water.

60. Compositions comprising an alpha-substituted benzaldoxime as active ingredient substantially as hereinbefore described with reference to the Table.

R. HALL
of REMFRY & SON,
Agent for the Applicants

Dated this 30th day of December 1960.

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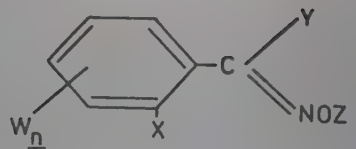

FIG. 1

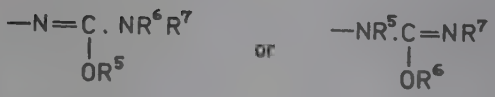

FIG. 2

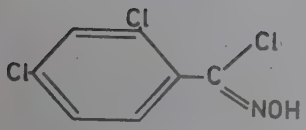

FIG. 3

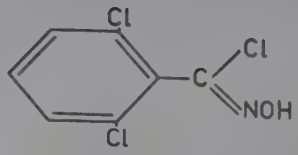

FIG. 4

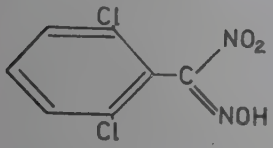

FIG. 5

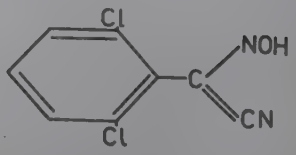

FIG. 6

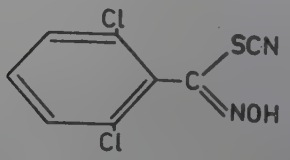

FIG. 7

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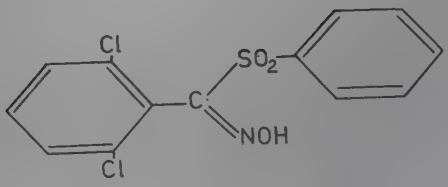

FIG. 8

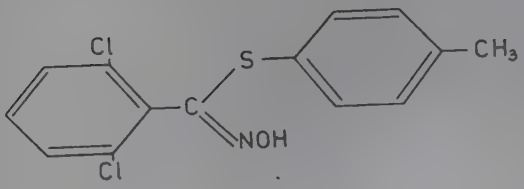

FIG. 9

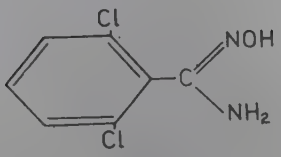

FIG. 10

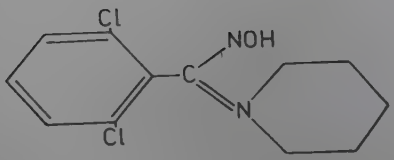

FIG. 11

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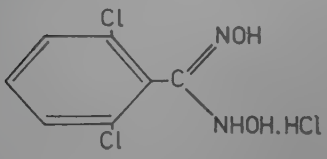

FIG. 12

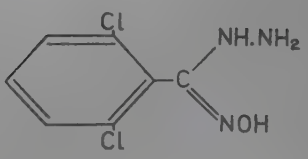

FIG. 13

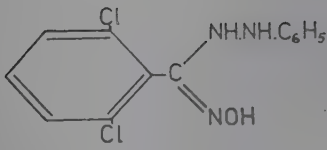

FIG. 14

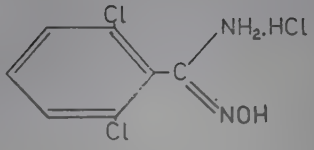

FIG. 15

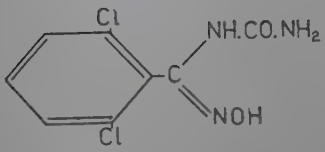

FIG. 16

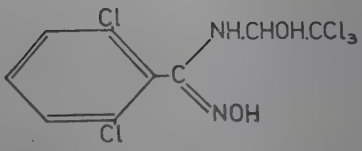

FIG. 17

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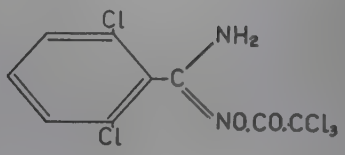

FIG. 18

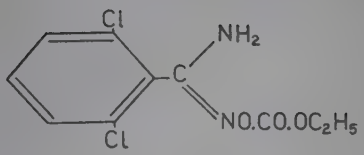

FIG. 19

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